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1,3-Alkadienes and their derivatives in reactions with electrophilic reagents

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ABSTRACT. **Literature data on the addition of electrophiles to 1,3-alkadienes and their derivatives have been reviewed. The chemo-, regio-, and stereo-selectivity of these reactions, mechanistic details, and their synthetic applications, are discussed.**

The bibliography contains 308 references.

Contents

I. Introduction 39
II. The addition of compounds with an electrophilic halogen atom 40
III. The addition of compounds with an electrophilic hydrogen atom 46
IV. The addition of compounds with an electrophilic carbon atom 47
V. The addition of compounds with an electrophilic atom of sulphur or its analogues 48
VI. The addition of compounds with an electrophilic nitrogen atom 51
VII. Conclusion 52

I. Introduction

The chemistry of 1,3-alkadienes has been a subject of close scrutiny during the last hundred years.[1–3] Work in this area has been stimulated in two ways: firstly by theoretical developments in organic chemistry, largely in connection with the ability of 1,3-alkadienes to participate in 1,4-conjugate addition; and, secondly, by the utilization of these compounds as monomers for the preparation of various forms of rubber and other synthetic materials.

The majority of the fundamental questions relating to the chemistry of 1,3-alkadienes were addressed within the first fifty years of this century. Experimentally, this has been achieved without the use of physical separation techniques or structure determination, and without attempting to gather authentic quantitative data. Therefore, in recent years, many reactions of 1,3-dienes, even well established ones, have been studied anew with the aid of chromatography, and IR- and NMR-spectroscopy. As a result, new data have been obtained for theoretical analysis.

Certain aspects of the chemistry of 1,3-alkadienes, for example halogenation, have been developed during the last ten years, notably for potential industrial application. The chlorination of 1,3-butadiene, and the subsequent dehydrochlorination of the resulting dichloride, has been known since the 1930's, and provides the basis of a new commercial route to chloroprene.[4]

As a result, a large amount of data on the chemistry of 1,3-alkadienes has been published, particularly in the last twenty years, and has not yet been reviewed in the literature or surveyed in monographs.

Reactions of 1,3-alkadienes with electrophiles are characteristic of this class of compound, which also undergo radical addition and participate in pericyclic processes, such as heterocyclisation (4+1), dimerisation and diene synthesis (4+2), and catalytic dimerisation (4+4).

Electrophilic addition to unsaturated compounds is a widely studied aspect of organic chemistry.[1–3] The majority of these reactions proceed by a two-step A_E2 mechanism. A carbenium or an onium ion is intermediate in the reaction depending on the nature of the substrate and electrophile. There is also reference in the literature to the possibility of there being other intermediates, notable uncharged species.[2,3] An alternative A_E3 mechanism has sometimes been invoked for this electrophilic addition.[1]

Electrophilic addition to 1,3-alkadienes follows the rules established for reactions of other alkenes. However, the presence of a further conjugated double bond has an effect on chemo-, regio- and stereo-selectivity.[5–9]

According to the general theory of electrophilic addition, the orientation of attack of the electrophile at the double bond should be such that the most stable intermediate is formed with delocalisation of the positive charge within an allylic system. The second stage, i.e. the addition of the nucleophilic residue, may proceed at one or other of the electrophilic centres depending on the electronic and steric environment of the conjugated system (inclusive of solvent and catalyst).

Electrophilic addition can be accompanied by substitution of hydrogen, usually at an unsaturated carbon atom, and in the case of 1,3-butadiene homologues there may be allylic substitution with rearrangement (Lvov–Tishchenko reaction). Although a detailed study of the mechanism of these reactions has not been undertaken, there is no doubt that an electrophilic mechanism is involved: the first stage is akin to aromatic substitution, and the second is a deprotonation characteristic of carbenium ions.

The information gathered and examined in earlier reviews and monographs has only been touched upon in this review. The bibliography contains references up to 1989. The chemistry of cycloalkadienes and carbon-functionalised alkadienes has not been included.

II. The addition of compounds with an electrophilic halogen atom

The following compounds contain an electrophilic halogen atom: halogens themselves, hypohalites (acids, esters and mixed anhydrides) and *N*-halides. All of these compounds can react with unsaturated compounds by a radical or electrophilic mechanism depending on their structure and the reaction conditions. In all cases, a direct indication of the mechanism of the reaction can be obtained from the chemo-, regio- and stereo-selectivity of the addition. All reported reactions of 1,3-dienes with *N*-halides proceed under conditions for radical addition,[10] and therefore have not been examined in this review.

1. Halogenation

Of all the electrophilic additions to 1,3-alkadienes, halogenation has been the most widely studied. It is normally carried out with free halogen (except fluorine) in an inert solvent (CH_2Cl_2, CCl_4 at -20 to 0 °C. Studies have been made of the interaction of 1,3-alkadienes with fluorine, chlorine, bromine and iodine, as well as with mixed halogens: FCl, FBr, ClBr and ClI. Detailed studies in this area have been carried out by V L Heasley et al. between 1970 and 1980.

The reaction of 1,3-butadiene with fluorine was reported for the first time in 1984.[11] The regioselectivity of the reaction depends on the nature of the fluorinating agent: with XeF_2 the 1,2-adduct predominates (87%), whereas with $PhIF_2$ the 1,4-adduct is favoured (64%). It is thought that reaction proceeds via a carbenium intermediate. Replacement of hydrogen by fluorine takes place as a side-reaction.

The interaction of 1,3-butadiene with chlorine was studied as long ago as 1886.[12] However, detailed information on the regioselectivity of the reaction was not available until 1930,[13] after which the reaction became the focus of numerous researchers.[14–27] Normally, 1,3-butadiene yields *trans*-1,4-dichloro-2-butene as the major product in preference to 3,4-dichloro-1-butene. However, if chlorination is conducted under non-radical conditions, the ratio of 3,4-dichloride to 1,4-dichloride is 2:1.[21] Both dichlorides undergo isomerisation on heating in the presence of $ZnCl_2$. At equilibrium, the mixture contains ~70%, 1,4-dichloro-2-butene.[18] In the presence of complex metal catalysts, e.g. copper naphthylate, the 1,4-dichloride isomerises to 3,4-dichloro-1-butene.[20]

By conventional chlorination of 1,3-butadiene the yield of dichlorides does not exceed 40% since significant amounts of tetrachloride are formed together with higher telomers. By adjusting the conditions of chlorination and using specific additives, in particular metal chlorides or various amines and phosphines, the yield of dichlorides can be raised to 97%.[23,24]

Several studies have been devoted to the kinetics of chlorination of 1,3-butadiene.[19,25–27] It has been shown that the formation of isomeric dichlorides follows a complex kinetic profile: 1,4-dichloro-2-butene by a second order process, and 3,4-dichloro-1-butene by a third order process. The activation parameters in the latter case would not suggest the formation of an ionic intermediate. From this it follows that the mechanism of addition of chlorine to 1,3-dienes is more complex than thought hitherto. It is possible that 1,4-addition proceeds to some extent by a radical pathway.[19,21]

Bromination of 1,3-butadiene is one of the most studied reactions of this compound.[14,28–41] The mechanism of addition of bromine depends on the dilution: at low concentrations (0.02 to 0.04 mol/l) it is electrophilic, while at high concentration a radical mechanism is involved.[36] Under conditions of electrophilic addition, 1,2-addition is observed to the extent of 57% in CCl_4 and 24% in CH_2Cl_2. *trans*-1,4-Dibromo-2-butene is formed predominantly (60%) under normal conditions. *cis*-1,4-Dibromo-2-butene has not been detected. 3,4-Dibromo-1-butene is converted slowly at room temperature, or rapidly on heating, to an equilibrium mixture containing ~80% *trans*-1,4-dibromo-2-butene. Thus, in contrast to the corresponding chlorides, the ratio of isomeric dibromides markedly depends on the conditions of bromination, notably the nature of the solvent.

In recent years, reference has been made to bromination of 1,3-butadiene with bromine complexes, e.g. dioxane dibromide,[39] pyridine dibromide, pyridinium tribromide,[40] and tetrabutylammonium tribromide.[41] In the first case, the ratio of addition products is approximately the same as that with molecular bromine. 3,4-Dibromo-1-butene is formed predominantly on bromination with pyridine dibromide, pyridinium tribromide and tetrabutylammonium tribromide. This indicates that the amine is involved in the transition state and/or the formation of an intermediate. The kinetics of bromination with Br_3^- has been studied in detail, and the distribution of electron density in the intermediate has been considered.[41]

Treatment of 1,3-butadiene with methyl hypochlorite and BF_3 in methylene chloride proceeds by 1,2- and 1,4-addition of FCl and methyl hypochlorite. The amounts of both types of adduct are approximately the same. In CCl_4 the yield of fluorochlorides, relative to methoxychlorides, rises significantly. The addition of FCl at the 1,2-position is strictly in accord with the Markovnikov rule, and is noticeably more dominant than 1,4-addition (with formation of *trans*-1-fluoro-4-chloro-2-butene). In CH_2Cl_2, the ratio of 1,2- to 1,4-addition is ~2:1, and in CCl_4 it is 3:1.[42]

Similarly, treatment of 1,3-butadiene with methyl hypobromite and BF_3 results in addition of FBr. The yield of fluorobromides in this case is less than that of bromoethers. The ratio of 1,2- and 1,4-adducts is 4:1.[42] It is thought that a complex, $BF_3Hal^+OR^-$, is formed during the reaction; this complexes with 1,3-butadiene to give an onium intermediate which then undergoes attack by both fluoride ion and methoxide.

The reaction of 1,3-butadiene with ClBr gives a mixture of 4-bromo-1-chlorobut-2-ene and 4-bromo-3-chloro-1-butene in 73:27 proportion.[43] With $Bu_4N^+BrCl_2^-$, only 1,2-addition of ClBr takes place; here, 84% of the product is formed according to the Markovnikov rule, and 16% contrary to this rule.[43,44] It is suggested that in this case reaction proceeds with formation of a three-centred intermediate with a delocalised positive charge; this is then attacked by chloride ion.

ICl adds to 1,3-butadiene with the formation of 1,4- and 1,2-adducts in 4:1 ratio. This is probably very close to the equilibrium product ratio.[45,46]

Iodination of 1,3-butadiene proceeds regioselectively with formation of *trans*-1,4-diiodo-2-butene.[47] Anionotropic systems with allylic iodine are extremely labile, and here reaction is clearly under thermodynamic control.

As a consequence, on passing from fluorine to iodine the amount of 1,4-adduct increases. Evidently, the determining factor here is the status of the system relative to that at equilibrium, i.e. the extent to which reaction is favoured by kinetic or thermodynamic control.[5]

The stereochemistry of addition of halogens to 1,3-alkadienes has been investigated with a view to assessing potential re-orientation and rotation in the transition state.[48] There is a possibility that addition of halogen results in formation of a non-ionic cyclic intermediate not requiring a significant degree of solvation. This accords with information gathered on the stereospecificity of this reaction.[35]

The regioselectivity of electrophilic chlorination of piperylene is markedly dependent on the geometry of the system and the polarity of the solvent. In CCl_4 *cis*-piperylene forms dichlorides (A), (B) and (C) in 29:20:46 proportion; in CH_2Cl_2 the proportion is 10:47:43. In CCl_4 *trans*-piperylene gives the same mixture of dichlorides in 4:47:49 proportion, while in CH_2Cl_2 the proportion is 2:66:32. Addition at the 3,4-position is stereospecific (89–95% *anti*).[48,49]

$$\underset{(A)}{MeCHCl{-}CHCl{-}CH{=}CH_2},$$

$$\underset{(B)}{MeCH{=}CH{-}CHCl{-}CH_2Cl},$$

$$\underset{(C)}{MeCHCl{-}CH{=}CH{-}CH_2Cl}.$$

Electrophilic bromination of piperylene proceeds predominantly with the formation of *trans*-1,4-dibromo-2-pentene.[50] 1,2-Addition at the disubstituted double bond (in the *anti*-mode) is much less, and minimal in the case of *trans*-piperylene. Thus, the halogen-onium complex at the terminal double bond, both on chlorination and bromination, is significantly more stable than the complex formed at the internal double bond.

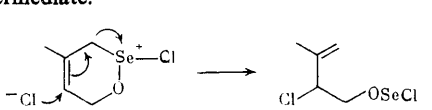
Chlorination of isoprene proceeds to a large extent by replacement of hydrogen by chlorine (Lvov–Tishchenko reaction) with the formation of 2-chloromethyl-1,3-butadiene.[21,51–55] Amongst the adducts which are also formed, 1,4-dichloro-2-methyl-2-butene (C) predominates.

$$\underset{\text{(A), 7\%}}{CH_2Cl{-}\overset{\overset{Me}{|}}{C}Cl{-}CH{=}CH_2}, \qquad \underset{\text{(B), 3\%}}{CH_2{=}\overset{\overset{Me}{|}}{C}{-}CHCl{-}CH_2Cl},$$

$$\underset{\text{(C), 49\%}}{CH_2Cl{-}C(Me){=}CH{-}CH_2Cl}, \qquad \underset{\text{(D), 49\%}}{CH_2{=}C(CH_2Cl){-}CH{=}CH_2}.$$

Other mono-chlorides are also reported to be formed on chlorination of isoprene. These may arise by dehydrochlorination of the dichloride adducts or may be products derived by 'aromatic' chlorination.[54] It is interesting to note that heating 1,4-dichloro-2-methyl-2-butene in the presence of a catalytic amount of copper(I) chloride and copper powder at 140 °C affords a mixture of comprising ~45% dichloride (B) and only ~3% dichloride (C).[53]

Chlorination of isoprene with $SeOCl_2$ in CH_2Cl_2 yields 1,4-dichloro-2-methyl-2-butene (in 39% yield) as a 2:1 mixture of *E*-and *Z*-isomers and 3-chloro-2-methyl-1-buten-4-ol (in 28% yield). The authors consider that the latter is formed by rearrangement of an intermediate:[55]



Bromination of isoprene has been reported extensively, as far back as 1898.[40,50,56–59] *trans*-1,4-Dibromo-2-methyl-2-butene is the major product, formed in 71% yield. The amount of 3,4-dibromo-3-methyl-1-butene in the mixture of dibromides is ~21%. *cis*-1,4-Dibromo-2-methyl-2-butene and 3,4-dibromo-2-methyl-1-butene are present in the mixture in small amounts (5 and 3%, respectively).

Bromination of isoprene with $SeOBr_2$ affords 1,4-dibromo-2-methyl-2-butene as a 2:1 mixture of *E*- and *Z*-isomers.[55]

ClBr adds to isoprene on treatment with $Bu_4N^+BrCl_2^-$ predominantly at the 1,2-position according to the Markovnikov rule.

$$\underset{78.6\%}{CH_2Br{-}\overset{\overset{Me}{|}}{C}Cl{-}CH{=}CH_2}; \qquad \underset{11\%}{CH_2{=}\overset{\overset{Me}{|}}{C}{-}CHCl{-}CH_2Br};$$

$$\underset{9.2\%}{CH_2Br{-}C(Me){=}CH{-}CH_2Cl}.$$

The addition of halogens to 2,4-hexadiene is of particular interest in relation to the stereochemistry of the reaction since this alkadiene exists as three geometric isomers. Their chlorination and bromination in a variety of solvents yields: *erythro*-4,5-dihalogeno-*cis*-2-hexenes, *threo*-4,5-dihalogeno-*cis*-2-hexenes, *dl*-2,5-dihalogeno-*trans*-3-hexenes, *meso*-2,5-dihalogeno-*trans*-3-hexenes, *threo*-4,5-dihalogeno-*trans*-2-hexenes and *erythro*-4,5-dihalogeno-*trans*-2-hexenes. The determination of the amount of each of these dihalides provides evidence in favour of the *syn*- or *anti*-character of the addition.[49,59]

In all cases, 1,4-addition is noticeably less on chlorination than on bromination. There is little information on solvent effects. These results are in accord with the findings of Farmer et al. more than 50 years ago,[31] and disprove a more recent report that the proportion of 1,2- and 1,4-adducts is independent of the polarity of the solvent.[35]

Chlorination and bromination of 2,3-dimethyl-1,3-butadiene[60–65] and 3-methyl-1,3-pentadiene[66] proceeds predominantly with the formation of *trans*-1,4-dihalides, and is associated with a significant degree of allylic substitution.

3,4-Addition takes place on chlorination and bromination of 1-aryl- and 1,4-diaryl-1,3-butadienes, while 1,4-addition is favoured on chlorination and bromination of 2-aryl-1,3-butadienes.[67,69]

Molecular-orbital calculations (LCAO approximation and others) have been carried out on several occasions with a view to examining the regioselectivity of addition to 1,3-butadiene and derivatives.[70,71]

All mono- and dichloro-1,3-butadienes, and notably polychloro-1,3-butadienes, undergo chlorination. Mkryan et al. have contributed most to this aspect. Data on reactions with other halogens is very limited.

Chlorination of 1-chloro-1,3-butadiene affords predominantly 3,4- and 1,4-adducts in addition to three of the possible substitution products:[72–74]

$$\underset{50.7\%}{CHCl{=}CH{-}CHCl{-}CH_2Cl}; \qquad \underset{5.9\%}{CHCl_2{-}CHCl{-}CH{=}CH_2};$$

$$\underset{12.1\%}{CHCl_2{-}CH{=}CH{-}CH_2Cl}; \qquad \underset{5.4\%}{CCl_2{=}CH{-}CH{=}CH_2};$$

$$\underset{1\%}{CHCl{=}CCl{-}CH{=}CH_2}; \qquad \underset{21.8\%}{CHCl{=}CH{-}CH{=}CHCl}.$$

According to another report, the proportion of 3,4- and 1,4-adducts is 1:1, which changes to 2:1 on addition of DMF to the solvent. In each case, 5–6% of the mixture comprises 3,4,4-trichloro-1-butene.[20]

A mixture of 3,4- and 1,4-adducts is formed on bromination of 1-chloro-1,3-butadiene.[73]

There are conflicting reports on the structure of the main product obtained by bromination of 1-bromo-1,3-butadiene. According to one reference the main product is 1,3,4-tribromo-1-butene,[45] and according to another it is 1,1,4-tribromo-2-butene.[75] In each case the structure of the product was assigned on the basis of ozonolytic data.

There are several publications on the chlorination of chloroprene.[76–81] All three of the possible trichlorobutenes are formed, but the 1,2- and 3,4-adducts are always in small amount:[79]

$$\underset{2.6\%}{CH_2Cl{-}CCl_2{-}CH{=}CH_2};\quad \underset{3.4\%}{CH_2{=}CCl{-}CHCl{-}CH_2Cl};$$
$$\underset{69.5\%}{CH_2Cl{-}CCl{=}CH{-}CH_2Cl};\quad \underset{20\%}{CHCl{=}CCl{-}CH{=}CH_2}.$$

The proportion of 1,2- and 3,4-adducts noticeably increases on addition of DMF to the solvent.[20] On chlorination in DMF the ratio of the three dichloride adducts shown above is 3 : 1 : 10.[80]

Bromination of chloroprene leads almost exclusively to 1,4-dibromo-2-chloro-2-butene. A trace of 3,4-dibromo-2-chloro-1-butene is also formed.[78]

ICl adds to chloroprene in an entirely different way: the 4,3-adduct, 2,3-dichloro-4-iodo-1-butene, is formed predominantly together with a trace of 4,1-adduct, 1,2-dichloro-4-iodo-2-butene:[78,81]

$$CH_2{=}CCl{-}CHCl{-}CH_2I;\quad CH_2Cl{-}CCl{=}CH{-}CH_2I.$$

Thus initial attack in this case is at the terminal C-atom of the non-chlorinated double bond. Below, it will be seen that bromination also takes place initially at the same carbon atom, while chlorination of chloroprene proceeds predominantly by attack at the terminal carbon atom of the chloro-substituted double bond.

Bromination of bromoprene takes place almost exclusively by 1,4-addition to give 1,2,4-tribromo-2-butene.[82]

Tables 1 and 2 summarise the results obtained by chlorination of all five dichloro-1,3-butadienes, two trichloro-1,3-butadienes, two tetrachloro-1,3-butadienes and one pentachloro-1,3-butadiene,[79–90] as well as a number of chloro-substituted isoprenes.[91–96] The preferential chlorination of the terminal, non-chlorinated, double bond is evident. Replacement of hydrogen by chlorine at the terminal methylene or methyl group takes place to a significant extent. There is no such substitution in the absence of terminal methyl or methylene groups.

3,4-Addition takes place on chlorination of 1-phenyl-4-chloro-1,3-butadiene, i.e. addition to the chlorine-substituted double bond.[96]

There is also reference in the literature to halogenation of certain halogeno-substituted 1,3-alkadienes, but without reliable information on the structure of the adducts (e.g. references[97,98]); these have been excluded from this review.

Halogenation of nitro-substituted 1,3-alkadienes has been rarely studied.[99] It is reported that bromine adds to 1-nitro-1,3-butadiene at the unfunctionalised double bond.[100] However, in more recent work it has been shown that 1-nitro- and 2,3-dimethyl-1-nitro-1,3-butadiene form 1,4-adducts with bromine.[101] Evidently, the latter can isomerise with rearrangement of the halogen to give the 3,4-adducts.

Dinitroalkadienes add bromine far more slowly than mononitro derivatives. 1,4-Dibromo-2,3-dimethyl-1,4-dinitro-2-butene is obtained by bromination of 2,3-dimethyl-1,4-dinitro-1,3-butadiene.[102]

Electrophilic halogenation is noticeably inhibited by phenyl substitution in the dinitroalkadienes. 1,4-Dinitro-1,4-diphenyl-1,3-butadiene does not give an adduct.

Bromination of 1-trimethylsilyl-1,3-butadiene gives a mixture of 3,4- and 1,4-adducts in equal amount.[103] The regioselectivity is the same as that observed on bromination of the all-carbon analogue, 4,4-dimethyl-1,3-pentadiene.

1,4-Dibromo-1-trimethylsilylbut-2-ene readily isomerises on heating with migration of bromine from the 1-position to the 3-position and from the 4-position to the 2-position. As a result, 3,4-dibromo-4-trimethylsilylbut-1-ene and 3,4-dibromo-1-trimethylsilylbut-1-ene are obtained.

Table 1. Chlorination of di- and poly-chlorobutadienes.

Chloro-substituted 1,3-butadiene	Products of chlorination	Content, %	Refs.
$CCl_2{=}CH{-}CH{=}CH_2$	$CCl_2{=}CH{-}CHCl{-}CH_2Cl$	69	[83]
	$CCl_2{=}CH{-}CH{=}CHCl$	31	
$CHCl{=}CCl{-}CH{=}CH_2$	$CHCl_2{-}CCl{=}CH{-}CH_2Cl$	*	[79]
$CHCl{=}CH{-}CCl{=}CH_2$	$CHCl{=}CH{-}CCl_2{-}CH_2Cl$	36/40**	[83]
	$CHCl_2{-}CH{=}CCl{-}CH_2Cl$	1/26**	
	$CHCl{=}CH{-}CCl{=}CHCl$	63/84**	
$CHCl{=}CH{-}CH{=}CHCl$	$CHCl_2{-}CHCl{-}CH{=}CHCl$	*	[83, 86]
$CH_2{=}CCl{-}CCl{=}CH_2$	$CH_2Cl{-}CCl{=}CCl{-}CH_2Cl$	*	[84, 85]
$CHCl{=}CCl{-}CCl{=}CH_2$	$CHCl{=}CCl{-}CCl_2{-}CH_2Cl$	71.5/66.2**	[87]
	$CHCl{=}CCl{-}CCl{=}CHCl$	28.6/28.7**	
$CCl_2{=}CCl{-}CH{=}CH_2$	$CCl_2{=}CCl{-}CHCl{-}CH_2Cl$	82	[88]
	$CCl_2{=}CCl{-}CH{=}CHCl$	18	
$CHCl{=}CCl{-}CCl{=}CHCl$	$CHCl_2{-}CCl{=}CCl{-}CHCl_2$***	*	[89]
$CCl_2{=}CCl{-}CCl{=}CH_2$	$CCl_2{=}CCl{-}CCl_2{-}CH_2Cl$	55	[87]
	$CCl_2{=}CCl{-}CCl{=}CHCl$	38.5	
$CCl_2{=}CCl{-}CH{=}CCl_2$	$CCl_3{-}CHCl{-}CCl{=}CCl_2$	72.8	[90]
	$CCl_2{=}CH{-}CCl_2{-}CCl_3$	27.2	

*One product isolated; **for *Z*- and *E*-isomers (given as a fraction); *** mainly the *cis*-isomer.

Thus, isomerisation leads in part to the formation of a dibromide which cannot be obtained by direct addition of bromine.

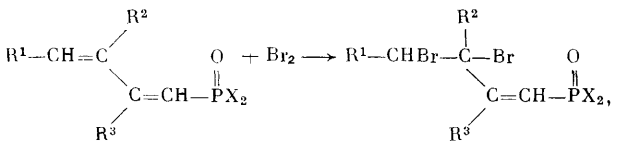
The isomeric ratio depends on the nature of the solvent and temperature: an increase in the solvent polarity and temperature favours the formation of the isomer having a silylated double bond.

The difference in the rate of bromination of 1-trimethylsilyl-1,3-butadiene and the all-carbon analogue suggests that the trimethylsilyl group exerts an electron-accepting activity relative to the tert-butyl group.[104]

Pudovik et al. established that chlorination of diethyl 1,3-butadiene-1-phosphonate takes place by attack at the non-phosphonated double bond.[105] More recently,[106] it was shown that bromination of both dialkyl 1,3-butadiene-1-phosphonates and the corresponding phosphonic acid chlorides also leads to the formation of the 3,4-adduct having the (*E*)-configuration.

Further studies on the interaction of 1,3-alkadiene-1-phosphonates with halogens has shown that various products result, depending on the preferred conformation of the 1,3-diene system. Thus, bromination of 1,3-alkadienephosphonates, prepared from PCl_5 and

the corresponding 1,3-alkadienes[107–109] and having, predominantly, the *S-trans*-conformation, proceeds with formation of 3,4-adducts:[110]



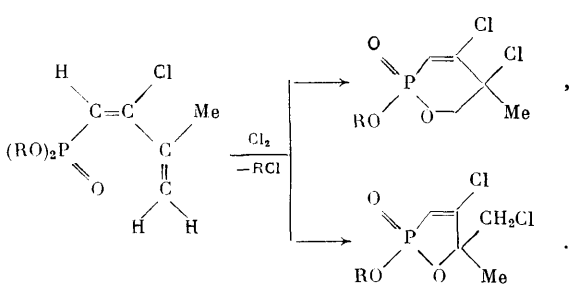
$R^1 = R^2 = R^3 = H$, Me; X = Cl, OMe, OEt.

Dehydrobromination with triethylamine leads to the corresponding 3-bromo-1,3-alkadienephosphonates.

Table 2. Chlorination of mono- and poly-chlorinated isoprenes.

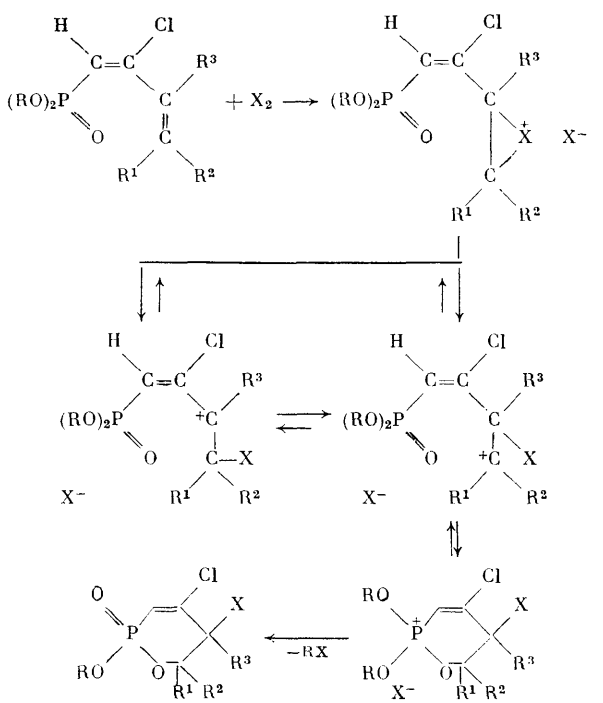
Chloro-substituted 2-methyl-chloro-1,3-butadiene	Chlorination products	Content, %	Refs.
$CHCl=C(Me)-CH=CH_2$	$CHCl=CMe-CHCl-CH_2Cl$	47	[91]
	$CHCl_2-CMe=CH-CH_2Cl$	33	
	$CHCl=CMe-CH=CHCl$	20	
$CH_2=C(Me)-CCl=CH_2$	$CH_2-C(Me)Cl-CCl=CH_2$	3.5	[92]
	$CH_2=CMe-CCl_2-CH_2Cl$	0.5	
	$CH_2Cl-CMe=CH-CH_2Cl$	55	
	$CH_2=C(CH_2Cl)-CCl=CH_2$	41	
$CH_2=C(Me)-CH=CHCl$	$CH_2Cl-C(Me)Cl-CH=CHCl$	38	[91, 93]
	$CH_2Cl-C(Me)=CH-CHCl_2$	30	
	$CH_2=C(CH_2Cl)-CH=CHCl$	12	
	$CHCl=C(Me)-CH=CHCl$	20	
$CH_2=C(Me)-CCl=CHCl$	$CH_2Cl-C(Me)Cl-CCl=CHCl$	19	[93, 94]
	$CH_2Cl-CMe=CCl-CH_2Cl$	24	
	$CH_2=C(CH_2Cl)-CCl=CHCl$	46	
$CH_2=C(Me)-CCl=CCl_2$	$CH_2Cl-C(Me)Cl-CCl=CCl_2$	36.8	[95]
	$CH_2=C(CH_2Cl)-CCl=CCl_2$	45.2	
	$CHCl=CMe-CCl=CCl_2$	18	
$Ph-CH=CH-CH=CHCl$	$Ph-CH=CH-CHCl-CHCl_2$	100	[96]

A mixture of 6- and 5-membered phosphorus-containing heterocyclics was obtained by chlorination of dialkyl 2-chloro-3-methyl-1,3-butadienephosphonates having predominantly the *S-cis*-conformation:[111–112]



The conversion to cyclic compounds is a consequence of a) the low energy of formation of such ring systems and b) the favourable transformation of the starting phosphonates into intermediates having a geometry which facilitates intramolecular nucleophilic attack by the phosphonyl group.[112,113] Chlorination of the corresponding 1,3-alkadienephosphonic dichloride does not effect cyclisation. Instead a complex mixture is obtained as a result of addition and dehydrochlorination of the adducts.[112]

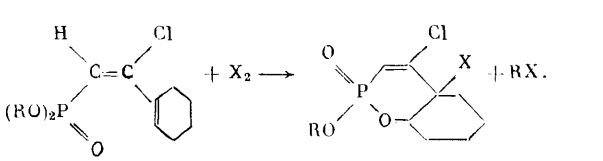
Halogenation of 2-chloro-3-alkyl-1,3-alkadienephosphonic acid esters having one or two substituents on the C_4 atom of the 1,3-diene system (which are obtainable via chlorination of the corresponding allenephosphonic acid dichlorides[114]) proceeds by heterocyclisation to yield 5,6-dihydro-2*H*-1,2-oxaphosphorins exclusively.[115,116] The highly selective interaction is due to the presence of an internal nucleophile (the phosphonyl group). This is attacked more readily by the electrophilic centre of the intermediate than by the anionic part of the reagent, thereby shifting the equilibrium towards formation of a stable six-membered phosphonium ion.[115]



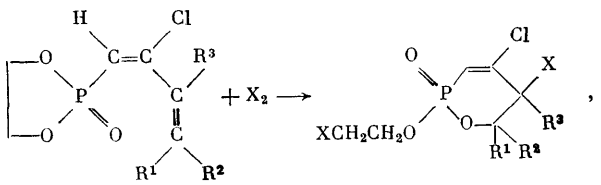
R = Me, Et, Pr, Pr^i, Bu; R^1 = H, Me4; R^2 = Me, Et; R^3 = Me, Et, Pr, Pr^i; X = Cl, Br.

Clearly, the preferential *S-cis*-conformation of the 1,3-diene system is particularly favourable for cyclisation.[117]

Halogenation[118,119] of dialkyl 2-chloro-2-(1-cyclohexenyl)-vinylphosphonates affords bicyclic *P,O*-containing heterocycles in which the C_3-C_4 double bond of the 1,3-diene system is incorporated in the ring.[118–120]

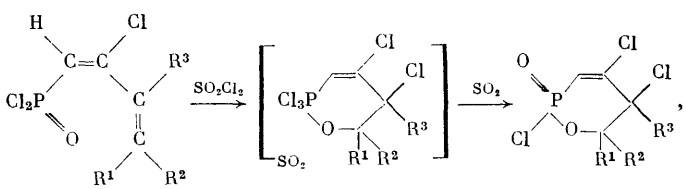


Halogenation of 2-(2-chloro-1,3-alkadienyl)-2-oxo-1,3,2-dioxaphospholanes proceeds in a similar way with associated cleavage of the dioxaphospholane ring and addition of halogen across the carbon-oxygen bond.[121]



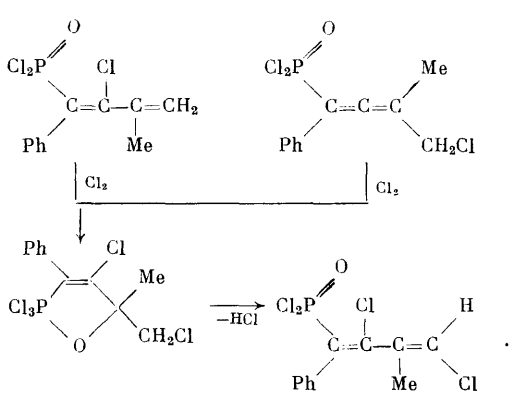
$R^1 = H$, Me; $R^2 = Me$; $R^3 = Me$, Et; X = Cl, Br.

Chlorination of 2-chloro-3-methyl-1,3-butadienylphosphonic acid dichloride with sulphuryl chloride yields a 3:1 mixture of the corresponding 5,6-dihydro-2*H*-1,2-oxaphosphorin and 2,5-dihydro-1,2-oxaphosphole.[122] However, 2-chloro-1,3-alkadienylphosphonic acid dichlorides with one or two substituents at the C_3 and C_4 positions give only a six-membered heterocycle under these conditions.[122]

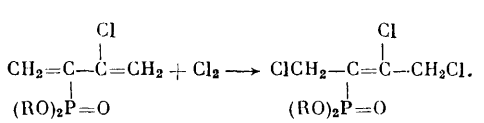


R^1 = H or Me; R^2 = H or Me, Et; R^3 = CH_3 or C_2H_5, C_3H_7.

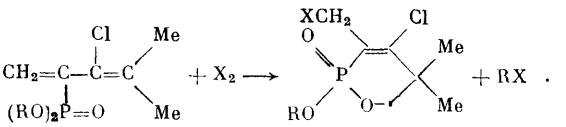
The interaction of 3-methyl-1-phenyl-2-chloro-1,3- and 3-methyl-1-phenyl-4-chloro-1,2-butadienylphosphonic acid dichloride with chlorine gives the same heterocycle, which eliminates HCl to give a dichloro-1,3-butadienylphosphonic acid dichloride.[123]



Halogenation of 3-chloro-1,3-alkadien-2-ylphosphonates gives a variety of products depending on the nature of the substituent at C_4 of the 1,3-diene system. Thus, interaction of dialkyl 3-chloro-1,3-butadien-2-ylphosphonates with chlorine leads to a 1,4-adduct.[124]



However, halogenation of 4-methyl-3-chloro-1,3-pentadien-2-ylphosphonic acid esters with two methyl groups at the 4-position yields 2,5-dihydro-1,2-oxophosphole derivatives.[124,125]



The geometry of the intermediate carbenium ion facilitates overlap of the unfilled orbital at the C_3-atom with the non-bonded orbitals of the phosphonyl group, leading to stabilisation of the entire system by ring closure.[124]

2. Addition of hypohalites

Hypohalites — hypohalous acids, their esters and mixed anhydrides — undergo addition to unsaturated compounds by a radical or ionic mechanism. In the latter case, reaction is conducted in dilute solution in the presence of radical inhibitors or in the presence of catalysts, such as BF_3, which facilitate electrophilic processes.

There is also the possibility of conjugate addition of hypochlorites to unsaturated compounds in hydroxylic solvents by using halogens, *N*-halogenamines and similar compounds with a positively polarised halogen atom. Under such conditions, the product obtained by addition of hypohalite contains a solvent molecule as well as halogen (solvo-adducts). Since the first step of the reaction (attack of the electrophile) is the same for both halogenation and conjugate hypohalogenation, the position of the halogen atom in the hypohalite adducts determines the direction of the initial attack in the first stage of halogenation. This reaction is important theoretically.

This reaction is also of significant synthetic value because it opens up a route to unsaturated epoxides, esters, carbonyl compounds, etc. The electrophilic addition of pre-formed hypohalites has only been studied in the hydrocarbon field. However, the products obtained by addition to 1,3-alkadienes are the same, irrespective of whether the hypohalite is pre-formed or formed *in situ*.

Conjugate addition of hypohalites to 1,3-alkadienes was studied systematically by A A Petrov et al. during the period 1935–1950.[126–129] 1,3-Butadiene, piperylene, isoprene and 2,4-hexadiene all undergo hypohalogenation. Various *N*-halogenamines and free halogen have been used as the halogenating agent. As a result of these studies, it has been established that hypohalites add predominantly at the 1,2-position, contrasting with addition of halogen and hydrogen halides. The proportion of 1,2- and 1,4-isomers is dependent on the method and the reaction conditions, as well as on the nature of the halogen.

Hydroxychlorination of 1,3-butadiene leads to the formation of the 1,2-adduct in 60–80% yield under various conditions.[126–131]

Alkoxyhalogenation of 1,3-butadiene also proceeds predominantly at the 1,2-position. As in the previously mentioned reaction, the regioselectivity depends on the method and temperature, the yield of 1,2-adduct being in the 80–90% range.[131–135] A 1,2-adduct is obtained in 62% yield by interaction of chlorine with a mixture of 1,3-butadiene and its mono-epoxide.[136]

Electrophilic addition of methyl hypochlorite to 1,3-butadiene in methanol affords 3-methoxy-4-chloro-1-butene in 70% yield. Approximately the same yield was obtained by treatment of methanolic 1,3-butadiene with chlorine, while radical addition of

methyl hypochlorite gives 4-methoxy-1-chloro-2-butene in 80% yield and the 1,2-adduct in 14% yield (contrary to the Markovnikov rule).[137]

Electrophilic addition of methyl hypochlorite to 1,3-butadiene in the presence of BF_3 gives a 37 : 17.5 mixture of chloroethers in CH_2Cl_2 and a 25 : 5.5 mixture in CCl_4. Fluorochlorobutenes are also formed, as has already been mentioned.[42]

Acoxychlorination of 1,3-butadiene with *N*-halogenamines in carboxylic acids gives a very small amount of ester, and the reaction has not been studied in detail.[126] Recently it was shown that the yield of acoxychlorides is significantly improved in the presence of $LiClO_4$; however, under these conditions the proportion of 1,4-adduct is increased markedly.[138]

Pre-formed acyl hypochlorites also add predominantly at the 1,2-position under electrophilic conditions.[21] The ratio of 1,2- and 1,4-adducts depends on the nature of the solvent: 2.8 : 1 in pentane, 2 : 1 in acetic acid, and 1.3 : 1 in acetonitrile.

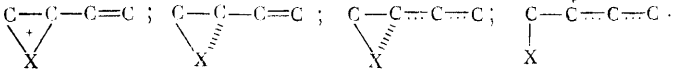
On hydroxy-, alkoxy- and acoxy-bromination of 1,3-butadiene with *N*-bromoamides, methyl hypobromite in the presence of BF_3, or with Br_2 in the appropriate hydroxylic solvent, the 1,4-adducts, if formed at all, are only obtained in small amounts; the corresponding bromoesters have not been isolated.[42,137,139,140]

The yield of 1,4-adduct is noticeably increased on acoxybromination with *N,N*-dibromobenzenesulfonamide in the presence of $LiClO_4$.[138] In contrast, alkyl hypobromites add exclusively at the 1,2-position in the presence of trimethyl borate.[141]

Only 1,2-adducts are obtained by hydroxy-, alkoxy- and acoxy-iodination of 1,3-butadiene with I_2/HgO in water or alcoholic media, or with iodoamides, e. g. NI_3, in acidic media.[142,143] The addition of pre-formed hypoiodites to alkadienes has not been studied.

The direction of the initial attack of halogen or hypohalite depends on the nature of the halogen atom; it is now thought that this directing influence is associated with the structure and stability of the intermediate onium ion.

It is conventional to represent the distribution of electron density in the intermediate by the following structures.[37]



The more the carbenium structure contributes to the intermediate ion, the more likely will reaction terminate by 1,4-addition. Kinetic and thermodynamic factors clearly play a leading role, being associated with the particular status of the system relative to that at equilibrium: on hypohalogenation under kinetic control, the less thermodynamically favourable 1,2-adduct is formed with a lower activation energy.[5]

Electrophilic addition of hypochlorous acid to piperylene leads to the formation of a mixture of 1,2-, 3,4- and 1,4-adducts in 47.1%, 39.7% and 13.2% yield respectively. The formation of the 3,4-adduct, which is contrary to the Markovnikov rule, requires further investigation.[144]

The interaction of piperylene with *N,N*-dichlorobenzenesulfonamide in methanol or ethanol proceeds by initial attack at the C_1-C_2 double bond to give, predominantly, a 5.6 : 4 mixture of 2-alkoxy-1-chloro-3-pentene and 4-alkoxy-1-chloro-2-pentene.[145]

The electrophilic interaction of piperylene with pre-formed hypochlorites (MeOCl) also provides a significant amount of 1,4-adduct. The yield of 1,2-, 1,4-, 4,1- and 4,3-adducts was 37–43%, 45–55%, 4–7% and 14–27%, respectively.[137]

It should be noted that the 3,4-adduct is formed in accordance with the Markovnikov rule, which is not the case for the addition of HOCl.[144]

2-Alkoxy-1-bromo-3-pentene and 4-alkoxy-1-bromo-2-pentene were obtained predominantly, in 5.6 : 4 proportion, by interaction of *N,N*-dibromobenzenesulfonamide with piperylene in alcoholic media (MeOH, EtOH).[146] Thus, as a general rule, alkyl hypobromites add to the 1,2-position to a greater extent than alkyl hypochlorites. However, in all cases piperylene forms much more of the 1,4-adduct. The reason for this is probably its rather high polarity.

Hypohalogenation of isoprene was first studied at the end of the last century.[56] More recently, reference has been made to the electrophilic addition of methyl and ethyl hypochlorite to isoprene in methanol and to the addition of tert-butyl hypochlorite in ethanol. A 3 : 2 mixture of 2-alkoxy-2-methyl-1-chloro-3-butene and 4-alkoxy-2-methyl-1-chloro-2-butene is formed in each case.[147] Other authors have reported slightly different ratios for these two products: 2 : 1 [148] and 3 : 1 [138] (with MeOCl), and 2.4 : 1 with EtOCl.[148] Small amounts of 3,4-adduct have also been reported.[148]

The interaction of isoprene with tert-butyl hypochlorite in acetic acid also leads primarily to the 1,2-adduct, which isomerises to the 1,4-adduct on treatment with acid.[147,149,150]

The 4,1-adduct is formed mainly if reaction is carried out in tert-butanol. This arises by radical addition of BuOCl to isoprene.

The addition of HOBr, alkyl hypobromites and alkyl hypoiodites to isoprene proceeds exclusively, or almost exclusively, at the 1,2-position.[148, 151, 152] This confirms that electrophilic bromination of isoprene is also initiated by attack at the C_1 atom.

The interaction of 1-tert-alkyl-substituted 1,3-butadienes with methyl hypoiodite (I_2, MeOH and HgO) leads to addition at the C_1-C_2 bond.[153]

Treatment of 1-phenyl-1,3-butadiene with dilute HOCl [154] and with HOBr [45] leads primarily to the 4,3-adduct. Later, the 1,2-adduct was also detected as one of the products.[155]

The study of reactions with halogeno-substituted alkadienes has revealed important mechanistic information on the addition of hypohalites to 1,3-dienes.

Hypohalites (HOBr, ROBr, ROI) add to 1-chloro- and 1-bromo-1,3-butadienes in the 4,3-mode.[14,156,157] Recently, an interesting reference was made to the conjugate chlorination of 1-chloro-1,3-butadiene in the presence of H_2O_2.[158] The reaction product is the hydroperoxide, $CHCl=CH-CH(OOH)CH_2Cl$.

Chloroprene and bromoprene add hypohalites in different ways depending on the nature of the halogen.

Contrasting with 1,3-butadiene, halogeno-1,3-alkadienes add HOCl and its esters predominantly at the 1,4-position; however 1,2-addition also takes place by attack at C_1 where the electron density is highest by virtue of the mesomeric effect of the halogen atom.[159] At the same time, reaction with HOBr or its esters and with HOI or its esters gives the 4,3-adduct almost exclusively with initial attack at C_4.[160–162] Clearly, these data would suggest that in the reactions of chloroprene and bromoprene with chlorine and iodine the direction of the initial attack is different.

Evidently, in both halogenation and hypohalogenation, the formation of an onium intermediate with participation of bromine and iodine is less facile in the presence of an electron-accepting C_1-C_2 bond. The intermediate is more stable if there is no halogen substitution of the double bond.

The recently reported conjugate addition of bromine and ethylene oxide to bromoprene is not in accord with the above. According to

the authors, reaction leads primarily to the formation of both types of 1,4-adduct as well as 3-bromethoxy-4-bromo-1-butene.[163]

1,2-Dichloro-1,3-butadiene adds methyl hypohalites at the unsubstituted double bond,[164] while 2,3-dichloro-1,3-butadiene gives both 1,2- and 1,4-adducts, the former predominating.[165]

1-Trialkylsilyl-1,3-alkadienes, just as the analogous all-carbon 1,3-alkadienes, add alkyl hypohalites only at the unsubstituted double bond (i.e. the non-silylated unsaturation) to give the 4,3-adduct.[166] The fact that the ratio of *cis*- and *trans*-isomers in the starting silyl-1,3-dienes and in the resulting 4,3-adducts is the same would suggest that an allyl-type carbenium ion is not formed in an intermediate step.

There is also reference in the literature to the formation of other solvo-adducts on halogenation of 1,3-butadiene. Thus, chlorination of 1,3-butadiene in DMF at −50 °C affords up to 70% of solvo-adducts as a mixture of two isomers which decompose at −10 °C:[167]

$$CH_2Cl{-}CH(OCH{=}N^+Me_2Cl^-){-}CH{=}CH_2;\quad CH_2Cl{-}CH{=}CH{-}CH_2OCH{=}N^+Me_2Cl^-.$$

III. The addition of compounds with an electrophilic hydrogen atom

Reagents in this category include hydrogen halides, hydroxylic compounds (water, alcohols, carboxylic acids) and mercapto compounds (hydrogen sulphide, thioalcohols, thioacids). Most of the data covering this aspect relates to the addition of hydrogen halides. Only the latter add to 1,3-dienes in the absence of catalyst, although in certain cases the use of a catalyst is necessary. An electrophilic mechanism is involved in the majority of reactions. Hydroxylic compounds add to 1,3-alkadienes only by an electrophilic mechanism in the presence of acid.

1. Hydrohalogenation

The hydrohalogenation of both 1,3-dienes and halogeno-1,3-dienes has been reported. There is reference to the addition of all four hydrogen halides to 1,3-alkadienes, but most of the data pertains to the reactions with HCl and HBr. A catalyst is required for the addition of HCl in non-aqueous media.

Table 3. Hydrochlorination of some chloro-substituted 1,3-alkadienes.

Chloro-substituted 1,3-alkadiene	Products of hydrochlorination	Content, %	Refs.
$CCl_2{=}CH{-}CH{=}CH_2$	$CCl_2{=}CH{-}CHCl{-}Me$	*	[196]
$CHCl{=}CCl{-}CH{=}CH_2$	$CCl_2{=}CCl{-}CHCl{-}Me$	*	[196]
$CH_2{=}CCl{-}CCl{=}CH_2$	$Me{-}CCl{=}CCl{-}CH_2Cl$	*	[84, 85]
$CH_2{=}C(Me){-}CH{=}CHCl$	$Me{-}C(Me)Cl{-}CH{=}CHCl$	74.6	[197]
	$CH_2{=}CMe{-}CHCl{-}CH_2Cl$	3.3	
	$CH_2Cl{-}CMe{=}CH{-}CH_2Cl$	8.6	
	$CHCl_2{-}CH{=}CMe_2$	13.5	
$CH_2{=}C(Me){-}CCl{=}CH_2$	$Me_2C{=}CCl{-}CH_2Cl$	49	[198]
	$CH_2Cl{-}CMe{=}CCl{-}Me$	33	
$CH_2{=}C(CH_2Cl){-}CCl{=}CH_2$	$(CH_2Cl)_2C{=}CCl{-}Me$	82	[92]
	$Me{-}C(CH_2Cl){=}CCl{-}CH_2Cl$	18	

* Only one product isolated.

1,3-Butadienes polymerise in the presence of HF.[168] Treatment with HCl in the presence of a catalyst (Cu_2Cl_2, $FeCl_2$, $FeCl_3$, $ZnCl_2$, $HgCl_2$) at room temperature in acetic acid, or without solvent at −80 °C, leads to a mixture of products containing 75−80% 3-chloro-1-butene and 20−25% 1-chloro-2-butene. The addition of peroxide has no effect on the course of the reaction. There is no interconversion of the two isomeric chlorides in the absence of catalyst, but on prolonged treatment with HCl or in the presence of catalyst (Cu_2Cl_2, $FeCl_3$) the mixture equilibrates to give ~25% 1,2-adduct.[169–171] Thus, on hydrochlorination the thermodynamically less stable isomer is present in far greater amount than in the equilibrated mixture. It is also reported that more than 96% of the 1,2-adduct is formed at low temperatures.[172]

The kinetics of the addition of HCl to 1,3-butadiene has been studied.[173] Electrophilic addition of HBr to 1,3-butadiene leads to the preferential formation of 1-bromo-2-butene. At equilibrium the mixture contains ~80% 1,2-adduct at −80 °C, and 80% 1-bromo-2-butene at 40 °C.[174,175] 1,2-Addition takes place to the extent of 65−90% in the absence of peroxide and at low temperatures.[175]

1-Iodo-2-butene is obtained by passing 1,3-butadiene through 57% HI at 20 °C.[169]

For the interaction of hydrogen halides with homologues of 1,3-butadiene, the direction of the initial electrophilic attack is in accord with the Markovnikov rule: the proton always adds to the terminal atom of the conjugated system since in this way the most stable (conjugated) carbenium ion is formed. For halogenation, there are a few exceptions to this rule. As seen in the tabulation above, small amounts of regioisomer may also be formed as a result of the two possible modes of cleavage of the halonium intermediate.

Because of the symmetry of the intermediate carbenium ion, hydrochlorination and hydrobromination of piperylene leads to the formation of only one halogenopentene isomer: 4-chloro- or 4-bromo-2-pentene. These may arise either by 1,2- or 1,4-addition of the hydrogen halide.[48,176,177] But, in fact, the 1,2-pathway is preferred. This is evident from a study of the interaction of *trans*-piperylene with DCl in a variety of solvents in the temperature range −78 to 25 °C. In all cases the 1,2-adduct is formed preferentially, i.e. 4-chloro-5-deuterio-2-pentene (62−78% of the mixture).[178]

The addition of HCl and HBr to isoprene has been studied by many authors.[179–183] Preferential 1,4-addition is reported, except in one instance[183] where 76−85% of the 1,2-adduct was isolated on hydrochlorination of isoprene at low temperatures under kinetic control.

Treatment of 2,4-hexadiene with HBr affords 90% of the 2,3-adduct,[179,184] while HCl and HBr react with 2,3-dimethyl-1,3-butadiene primarily by 1,4-addition.[46,179]

A special note should be made of the addition of HCl to the third isomer of dimethylbutadiene, namely 4-methyl-1,3-pentadiene.[88] Here, the product is reported to be 4-chloro-4-methyl-1-butene. Thus, if this information is correct, then it is the only example which is not in accord with the general rule mentioned above: that the proton adds only to the terminal carbon atom of the conjugated system. With 4-methyl-1,3-pentadiene, the intermediate carbenium atom is evidently stabilised by hyperconjugation with the C−H bonds of the two methyl groups.

Hydrochlorination and hydrobromination of 1-phenyl-1,3-butadiene leads to the 4,3-adducts, i.e. 1-phenyl-3-halogeno-2-butenes.[185,186]

1-Chloro-1,3-butadiene adds HCl at −10 to −15 °C in the presence of Cu_2Cl_2 to give primarily 1,3-dichloro-1-butene (73%

4,3-adduct) together with a mixture of 1,1-dichloro-2-butene and 1,4-dichloro-2-butene (in 15% yield).[187] A catalyst, e.g. $AlCl_3$ or $FeCl_3$, is necessary for this reaction in non-aqueous media.[188]

1,3-Dihalogeno-2-butenes are formed predominantly by interaction of chloroprene or bromoprene with HCl or HBr in the presence of copper halides.[189–194] The reaction of bromoprene with HCl, either in the presence or absence of Cu_2Cl_2, is accompanied by isomerisation and halogen exchange to give 3% of the 2,1-adduct.[195] The formation of a small amount of primary carbenium ion is possibly associated with the participation of the halogen atom in the conjugated system.

The hydrochlorination of a numbr of dichlorobutadienes and mono- and dichloro-isoprenes is summarised in Table 3.

It is clear from the tabulation that addition of HCl takes place preferentially at the unfunctionalised double bond.

The replacement of the hydrogen atoms of the methyl group by chlorine lowers its electron-donating properties in relation to the conjugated double bond system, and the mesomeric effect of a chlorine atom at the other double bond has a clear effect on the orientation of attack by the proton.

1,2-Dichloro-1,3-butadiene adds HBr at the unchlorinated double bond in accordance with the Markovnikov rule,[198] and 2,3-dichloro-1,3-butadiene affords the 1,4-adduct.[85]

Hydrobromination of 1-phenyl-4-chloro-1,3-butadiene takes place at the 4,3-position, i.e. by attack of proton at the terminal carbon atom of the chlorinated double bond.[45]

2. Addition of water, alcohols and organic acids

The reactions of 1,3-alkadienes with hydroxyl-containing compounds have not been extensively studied, although they are of significant interest as methods of preparing unsaturated alcohols and ethers. Certain of the latter may serve as suitable synthons in, for example, the synthesis of natural products and their analogues.

Diacetyl has been obtained by addition of water to 1,3-butadiene in the presence of Hg^{2+} and acid.[199,200]

The initial stage of formation of diacetyl involves addition of methanolic mercuric acetate to 1,3-butadiene according to the following scheme.[201]

$$CH_2=CH-CH=CH_2 \xrightarrow[MeOH]{Hg(OCOMe)_2}$$

$$\rightarrow MeCOOHg-CH_2-CH(OMe)-CH(OMe)-CH_2-HgOCOMe \xrightarrow{2I_2}$$

$$\rightarrow CH_2I-CH(OMe)-CH(OMe)-CH_2I \xrightarrow[-2HI]{} CH_2=\underset{\displaystyle OMe}{\underset{|}{C}}-\overset{\displaystyle OMe}{\overset{|}{C}}=CH_2 \rightarrow$$

$$\xrightarrow[H_2O]{H^+} MeCO-COMe.$$

A mixture of 1,2- and 1,4-adducts was obtained by hydration of 2-alkyl-1,3-butadienes in the presence of mineral acid. Hydration of isoprene gives primarily 3-methyl-1-buten-3-ol.[202]

The addition of water to 1-phenyl-1,3-butadiene in the presence of acid, under kinetic control, proceeds with initial protonation of the C_4 atom and formation of a mixture of isomeric alcohols (4,3- and 4,1-adducts).[203]

A kinetic study has been made of acid-catalysed hydration of 1,3-butadiene, chloroprene, bromoprene, and 2-phenyl-1,3-butadiene.[202]

Addition of acetic and propionic acid to 1,3-butadiene in the presence of perchloric acid affords mainly the 1,4-adduct. Telomerisation takes place simultaneously with the formation of esters having two or more linearly bonded butene residues.[204]

$$CH_2=CH-CH=CH_2 \xrightarrow[HClO_4]{MeCOOH}$$

$$\longrightarrow H-[CH_2-CH=CH-CH_2]_n-OCOMe.$$

In the case of acetic acid, the yield of 1,4-adduct (n = 1) is ~15% and that of the telomer (n = 2) is ~35%. Isomeric esters were also isolated in trace amounts as a result of telomerisation of the corresponding isomeric carbenium ions. Several patents have been published on this process, e.g. Ref. 205.

The addition of acetic acid to isoprene in the presence of $HClO_4$ proceeds mainly by 1,4-addition and is accompanied by telomerisation.[206] This reaction has been applied to the synthesis of prenyl acetate, aliphatic terpenes, sesquiterpenes, etc., notably geranyl acetate and farnesyl acetate.

Hydration of chloroprene in the presence of acid proceeds predominantly by 1,4-addition with the formation of 3-chloro-2-buten-1-ol.[192] More recently, it has been shown that methyl vinyl ketone is formed as a by-product in small amounts, i.e. 1,2-addition also takes place.[202]

3. Addition of thiols

Thiols and mercapto-containing compounds in general add to unsaturated hydrocarbons and their derivatives primarily by radical and nucleophilic mechanisms. Electrophilic addition does not normally take place. However, reference has been made to the electrophilic addition of thiols to 1,3-dienes in the presence of catalytic amounts of $HClO_4$.[207] In this way, 1,4-adducts are formed preferentially (> 80% yield). With unsymmetrical alkadienes proton attack takes place at the terminus having the most nucleophilic carbon atom to give the corresponding carbenium ion.

$$CH_2=\underset{\displaystyle Me}{\underset{|}{C}}-CH=CH_2 \xrightarrow{H^+} Me_2\overset{+}{C}-CH=CH_2 \longrightarrow$$

$$\xrightarrow{RSH} Me_2C=CH-CH_2SR,$$

$$CH_2=\underset{\displaystyle Me}{\underset{|}{C}}-CH=CH-Me \xrightarrow{H^+} Me_2\overset{+}{C}-CH=CH-Me \longrightarrow$$

$$\xrightarrow{RSH} Me_2C=CH-CHSR-Me\ .$$

Reaction with 2-methyl-1,3-pentadiene is more facile than with isoprene, as would be anticipated for electrophilic addition.

IV. Addition of compounds with an electrophilic carbon atom

Organic halides add to a multiple bond only in the presence of a Friedel-Crafts-type catalyst. Acyl halides and α-halogenoethers are the most reactive.

1. Addition of alkyl and alkenyl halides

The first reference to the addition of alkyl and alkenyl halides to 1,3-alkadienes was made in a French patent in 1938.[208] This reaction was studied in detail by Leets and A A Petrov et al., commencing in 1954.[209–213,215–223] In the addition to unsaturated halogeno derivatives, satisfactory yields were only obtained by reaction with tertiary alkyl halides. The latter add in the 1,4-position, reaction being accompanied by telomerisation, i.e. 1:1 adducts are formed together with 2:1, 3:1, etc. adducts. Most reactions have been carried out in the presence of $SnCl_4$ as catalyst, although improved yields may be obtained with $BiCl_3$.[214] The regioselectivity of addition to unsymmetrical alkadienes is the same as that with hydrogen halides. The products of these reactions have been widely used in the synthesis of unsaturated hydrocarbons, carbonyl compounds, carboxylic acids, and various heterocyclics.[211]

The reaction between 1,3-alkadienes and allylic halides is synthetically the most interesting, notably the reaction of isoprene with isoprene-HCl adducts.[215,216] In this case, a mixture of 1:1 adducts is obtained, comprising geranyl chloride (52–56%), linalyl chloride (7–8%), lavandulyl chloride (9–10%), α-terpenyl chloride (18–20%) and prenyl chloride dimers (9–10%).[217] Farnesyl chloride is one of the components of the fraction containing a 2:1 mixture of telomers.[218–200] This compound can also be obtained by reaction of isoprene with geranyl chloride.[221,222]

The above-mentioned reaction has been applied in recent years to the synthesis of various natural compounds and their analogues, including vitamins, hormones and insecticides.

Studies have also been made of the products formed by telomerisation of other alkadienes with various allylic chlorides. Thus, a number of homologues, isomers and analogues of natural terpenes have been obtained.

2-Chloro-1,3-butadiene adds alkyl and alkenyl halides in the 1,4-position, the regioselectivity being the same as with HCl.[223]

2. Addition of halogenoethers

The study of the reaction between 1,3-dienes and α-halogenoethers in the presence of Friedel–Crafts catalysts was undertaken much earlier than that with other organic halides.[224] This reaction was investigated in detail by Pudovik between 1945 and 1949.[225–227] Catalytic activity decreases in the following order: $ZnI_2 > ZnBr_2 > ZnCl_2 > HgCl_2 > Cu_2Br_2 > PdCl_2 > CoCl_2$. Ethers of the type ArCH(Hal)OMe react with alkadienes without a catalyst. A mixture of 1,2- and 1,4-adducts is obtained from 1,3-butadiene, the former comprising 75–80% if isomerisation is prevented. At equilibrium the mixture contains 75% of 1-methoxy-3-pentene.

Isoprene affords 1,4-adducts predominantly, i.e. 4-alkoxy-1-chloro-2-methyl-2-butenes.[227] The reaction of 1,3-alkadienes with α-chloroalkyl acetates leads to alcohols following 1,4-addition.[228] The reaction of alkadienes with cyclic α-chloroethers proceeded in the same manner.[229–231] 4-Alkoxy-1,3-dichloro-2-butenes were chiefly obtained by treatment of chloroprene with α-chloroethers, i.e. the regioselectivity of the reaction is the same as that with hydrogen halides.[232,233] Tetrahydropyran derivatives were mainly formed by reaction of alkadienes with α,α-dichloroalkyl ethers.[234] The products obtained by reaction with α-halogenoethers have been used synthetically in a variety of ways, e.g. in the synthesis of juvenile hormones and insecticides.[211,234–236]

3. Addition of acyl halides

The reactions of unsaturated compounds with acyl halides with Friedel–Crafts catalysts were first studied in the 1960s.[211,237,238]

It was not until several years later that Badanyan et al. reported the successful chloracylation of alkadienes, e.g. isoprene, chloroprene, isomeric dichlorobutadienes and other alkadienes.[239–243] Acyl halides add to alkadienes in the presence of $AlCl_3$ at −78 °C to give ethylenic ketones of the type $RCOCH_2CX=CHCH_2Cl$, which readily dehydrochlorinate with triethylamine to give primarily *cis*-2,4-dienones of the type (*E*)-$RCOCH=CX-CH=CH_2$.[240,241] Dehydrochlorination can take place during the reaction.

Unsaturated aromatic ketones are obtained by chloroacylation of 1,3-alkadienes and their halogen-containing derivatives in the presence of aromatic compounds:[243]

$$CH_2=CX-CX=CH_2 \xrightarrow[AlCl_3]{MeCOCl,\ PhR} Me-CO-CH_2-CX=CX-CH_2-C_6H_4R.$$

Dibasic dicarboxylic acid chlorides (derived from suberic, azelaic and sebacic acids) react similarly with 1,3-butadiene and chloroprene under the same conditions. The products formed by double addition readily dehydrohalogenate with triethylamine to give (*E,E*)-diketotetraenes of the type $[CH_2=CH-CX=CHCO(CH_2)_n]_2$.[242]

Acylation of 1,3-butadiene with acetyl fluoroborate in the presence of acetic anhydride (in 1:1 proportion) leads to the formation of 1,2- and 1,4-solvo-adducts, namely (*E*)-3-acetoxy-1-hexen-5-one (by 1,2-addition) and 1-acetoxy-2-hexen-5-one (by 1,4-addition), respectively, in 1:8 proportion.[244,245]

$$CH_2=CH-CH=CH_2 \xrightarrow[(MeCO)_2O]{MeCO^+,\ BF_4^-} \begin{cases} \rightarrow Me-CO-CH_2-CH(OCOMe)-CH=CH_2, \\ \rightarrow Me-CO-CH_2-CH=CH-CH_2OCOMe. \end{cases}$$

The addition of acetyl fluorosulfonate to alkadienes provides a potential synthetic route to acyl-1,3-alkadienes.[246] The latter are obtained by treatment of the adducts with triethylamine. If the dehydrohalogenation is carried out in methanol, the corresponding solvo-adducts are formed, i.e. β-alkoxy-γ,δ-ethyleneketones.

$$CH_2=CH-CH=CH_2 \xrightarrow{Me-CO-OSO_2F} Me-CO-CH_2-CH(OSO_2F)-CH=CH_2$$

$$\xrightarrow{Et_3N} Me-CO-CH=CH-CH=CH_2, \qquad \xrightarrow{Et_3N,\ MeOH} Me-CO-CH_2-CH(OMe)-CH=CH_2.$$

V. The addition of compounds with an electrophilic atom of sulphur or its analogues

Organosulphur compounds with the sulphur atom in all three valence states may participate in electrophilic addition or substitution of 1,3-alkadienes. Most of the data in this area relates to the reactions of 1,3-alkadienes with sulphenyl chlorides, RSCl. However, reactions with sulphinyl chlorides, sulphonyl chlorides and SO_3 are also known.

1. Addition of sulphenyl halides and their analogues

Reactions of unsaturated compounds with sulphenyl halides and their analogues have already been the subject of a review.[247] They all proceed by electrophilic attack with the intermediate formation of an episulphonium ion.[248,249] With unsymmetrical olefins, adducts may arise in accordance with, and contrary to, the Markovnikov rule, the Markovnikov products predominating under kinetic control. These reactions are more facile in polar media, and are characterised by *trans*-addition.

Studies have been made of the reactions of sulphenyl chlorides with 1,3-alkadienes, their halogeno- and trialkylsilyl-derivatives, and with 1,3-alkadienylphosphonates. 1,2-Addition or 3,4-addition takes place in all cases, either exclusively or predominantly.[250–257] As is evident from Table 4, sulphenyl ion initially attacks 1-alkyl- or 1-aryl-derivatives at the 4-position, 2-methyl-derivatives at the 1-position, and 2-phenyl-derivatives at the 4-position. The rate of addition can vary by factors of ten.[252]

The nature of the solvent has a pronounced effect on the regioselectivity of addition. Thus, in acetic acid, isoprene and *p*-chlorobenzenesulphenyl chloride give 1,2-, 4,3- and 4,1-adducts in 20:20:60 proportion, while in nitromethane the ratio is 61:18:21, in THF it is 33:27:40, and in CCl_4 it is 63:22:15.[253]

The 1,2-adducts readily isomerise, even at room temperature, to give the thermodynamically more stable 1,4-adducts. At equilibrium the mixture contains more than 90% of the 1,4-isomer. The rate of isomerisation increases on heating in the presence of sulphuric acid as catalyst. The nature of the substituent on the sulphur atom influences the rate of isomerisation. Thus, the products obtained by addition of PhSCl isomerise less than those obtained with MeSCl.[251]

Acetylthiosulphenyl chloride (MeCOSSCl) adds to 1,3-butadiene in the same manner at −20 °C in CH_2Cl_2. With piperylene, addition takes place preferentially (82%) at the mono-substituted double bond.[255]

Dimethyl and diphenyl disulphide undergo 1,4-addition with 1,3-butadiene in the presence of boron fluoride. Reaction also proceeds via an episulphonium intermediate, although in the presence of a catalyst rearrangement takes place.[256]

Diethoxyphosphorylsulphenyl chloride adds to 1,3-butadiene to give the 1,2-adduct in accordance with the Markovnikov rule.[257]

p-Chlorobenzenesulphenyl chloride adds to 1-chloro-1,3-butadiene at the unfunctionalised double bond.[253]

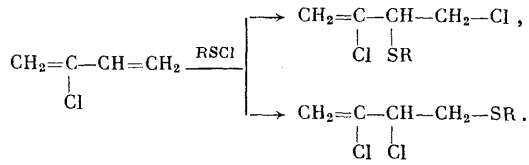
The reaction of methyl- and *p*-chlorobenzene-sulphenyl chloride with chloroprene proceeds chemo- and regio-selectively. Attack takes place at the more nucleophilic C_3-C_4 double bond with the

Table 4. Addition of *p*-chlorobenzenesulfenyl chloride to 1,3-alkadienes.

1,3-Alkadiene	Temperature, °C	Solvent	Reaction products	Content, %	Refs.
$CH_2=CH-CH=CH_2$	25	$C_2H_2Cl_4$	$ArS-CH_2-CHCl-CH=CH_2$	>95	[252]
$CH_2=CH-CH=CH-Me$	»	»	$ArS-CH_2-CHCl-CH=CH_2$	73/60*	[252]
			$CH_2=CH-CHCl-CH-SAr-Me$	24/35*	
$CH_2=C(Me)-CH=CH$	»	»	$ArS-CH_2-CMeCl-CH=CH_2$	72	[252]
			$CH_2=CMe-CHCl-CH_2SAr$	23	
$CH_2=C(Me)-C(Me)=CH_2$	»	»	$ArS-CH_2-CMeCl-CMe=CH_2$	см. 2*	[252]
$CH_2=CH-CH=CMe_2$	»	»	$ArS-CH_2-CHCl-CH=CMe_2$	см. 2*	[252]
$CH_2=CH-C(Me)=CH-Me$	»	»	$ArSCH_2-CHCl-CMe=CH-Me$	53[3]*	[252]
			$CH_2=CH-CMeCl-CH(SAr)-Me$	45[3]*	
$Me-CH=CH-CH=CH-Me$	»	»	$ArS-CHMe-CHCl-CH=CH-Me$	>95[4]*	[252]
(*E*) $CH_2=C(Me)-CH=CH-Me$	»	»	$ArS-CH_2-CMeCl-CH=CH-Me$	73	[252]
			$CH_2=CMe-CHCl-CH(SAr)-Me$	22	
(*E*) $PhCH=CH-CH=CH_2$	20	CCl_4	$Ph-CH=CH-CHCl-CH_2SAr$	см. 2*	[253]
$CH_2=C(Ph)-CH=CH_2$	»	»	$CH_2=CPh-CHCl-CH_2SAr$	20	[253]
			$CH_2Cl-CPh-CH-CH_2SAr$	80	
$CH_2=C(Ph)-C(Ph)=CH_2$	»	»	$CH_2ClCPh=CPh-CH_2SAr$	см. 2*	[253]

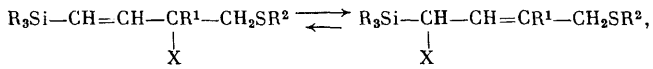
* The first number refers to the yield from the *Z*-isomer, and the second number from the *E*-isomer; [2]* only one isomer isolated; [3]* the yield was almost the same from either *E*- or *Z*-isomer; [4]* the *Z*-adduct was formed from the *Z,Z*-isomer; the *Z*/*E* proportion was ≃28:67 from the *Z,E*-isomer, and ≃22:73 from the *E,E*-isomer.

predominant formation of the Markovnikov adduct (74–94%) and 6–26% of the anti-Markovnikov adduct.[255]



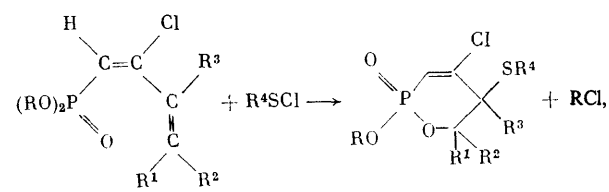
The addition of alkylsulphenyl halides (chlorides and bromides) to 1-trialkylsilyl-1,3-dienes takes place at the non-silyated double bond in accordance with the Markovnikov rule, i.e. formation of 4,3-adducts.[258]

The high regioselectivity is evidently a consequence of increased steric hindrance at the silylated double bond. It is also probable that the addition at the 4,3-position is facilitated by the increased stability of the episulphonium ion at the unfunctionalised double bond relative to that at the C_1-C_2 double bond due to $d_\pi-p_\pi$ interaction. The resulting 4,3-adducts undergo allyl rearrangement on heating (distillation) with migration of halogen from tertiary to primary carbon atom.[258]



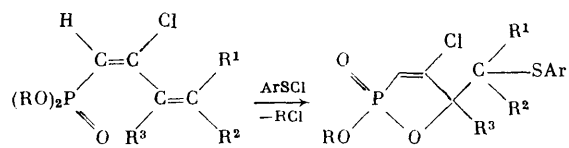
R = Me, Et; R^1 = H; Me; R^2 = Me, Et; X = Cl.

Sulphenyl chlorides react with phosphorylated 1,3-alkadienes at the C_3-C_4 double bond, as is the case with addition of halogens (as mentioned earlier). A 5- or 6-membered heterocycle is then formed depending on the nature of the sulphenyl chloride. This interaction is not regioselective since a number of conformers are involved in the reaction.[259] With alkylsulphenyl chlorides, the *cis*-conformer of the alkadienylphosphonate is involved.



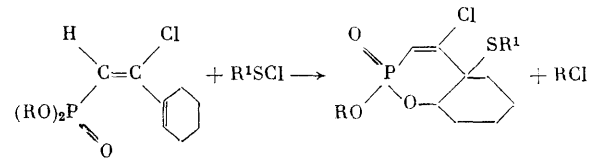
R^4 = Me, Pr^i.

Because of steric hindrance by substituents, the interaction with arylsulphenyl chlorides involves the *S-trans*-conformer, which leads to 2,5-dihydro-1,2-oxaphospholes:[259]



Ar = Ph, *p*-MeC_6H_4.

The interaction of 2-chloro-2-(1-cyclohexenyl)vinylphosphonates with sulphenyl chlorides affords hexahydrobenz-2*H*-1,2-oxaphosphorines, irrespective of the nature of the substituent on the sulphur atom.[260]



R^1 = Me, Pr^i, Ph, *p*-MeC_6H_4.

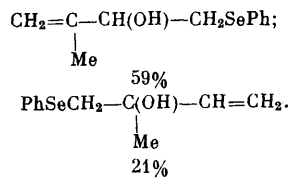
The fact that 6-membered bicyclic *P,O*-heterocyclics are formed predominantly, irrespective of the nature of the organic residue (on sulphur), can be explained, in part, by the stability of the *S-cis*-conformer of the starting dienephosphonate and, in part, by the probable increased stability of the intermediate involved in formation of the bicyclic compound relative to that of the spirocyclic intermediate which would arise if a 5-membered *P,O*-heterocycle were formed.

Phenylselenenyl chloride adds to isoprene both at the 1,2- and 4,3-positions. The ratio of the adducts is 1:1 at 0 °C and 5:2 at 60 °C.[261]

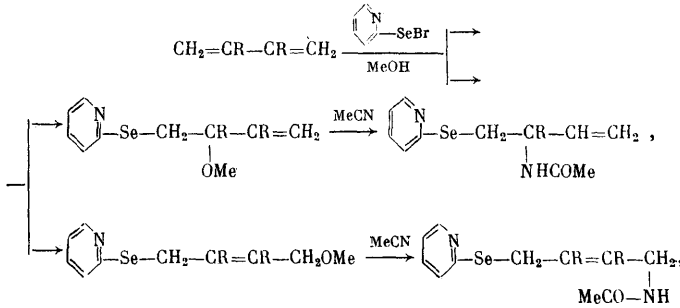
Alkylselenenyl chlorides add to *Si*-containing 1,3-alkadienes only at the unfunctionalised double bond, in the same manner as alkylsulphenyl chlorides. Here, the electrophile (RSe^+) attacks C_4 of the conjugated system to give the corresponding 4,3-adducts.[262]

The interaction of 1,3-alkadienes with selenenyl chlorides may also lead to solvo-adducts,[263] as is the case with halogenation (see earlier). Hydroxyl-containing selenoethers are obtained by reaction of PhSeCl with 1,3-butadiene, isoprene, and 2,3-dimethyl-1,3-butadiene in acetonitrile-THF in the presence of water.

With isoprene, addition takes place predominantly at the monosubstituted double bond. 1,4-Adducts are not formed.



The interaction of 1,3-butadiene and 2,3-dimethyl-1,3-butadiene with 2-pyridylselenenyl bromide in methanol and acetonitrile proceeds in a similar way in the presence of CF_3SO_3H, although here solvo-adducts of a different type are formed.[264] With 1,3-butadiene, the ratio of 1,2- and 1,4-adduct was 67:33, while 2,3-dimethyl-1,3-butadiene gave only the 1,4-adduct.



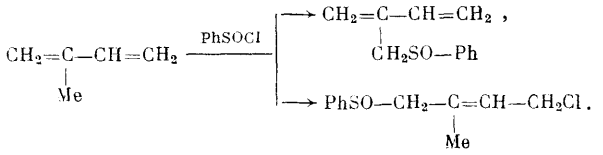
R = H or Me.

As 1,2-adducts readily isomerise into 1,4-adducts, the latter may arise via isomerisation of initially-formed 1,2-adducts.

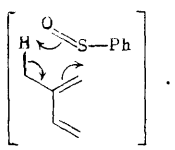
The interaction of 1,3-alkadienes with $PhSeCl_3$ has also been studied.[265] 1,3-Butadiene affords 2-chloro-3-butenyl(phenyl)selenide dichloride, which can be converted to chloroprene on hydrolytic removal of the selenium function. Isoprene gives a mixture of 1,2- and 4,3-adducts in 1 : 1 proportion.

2. Reactions with oxygen-containing sulphur compounds

The interaction of 1,3-alkadienes with benzenesulphinyl chloride has only been studied in the case of isoprene.[266,267] Reaction proceeds predominantly by sulphinylation, but the mechanism of the conversion has not yet been established with certainty.

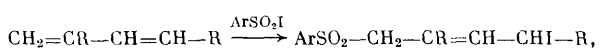


It is thought that sulphinylation takes place by an ene-type reaction through the following transition state:



Reactions of 1,3-alkadienes with aromatic sulphonyl halides has been studied widely. In the majority of cases, reaction proceeds in the presence of a catalyst, notably copper halides, by a radical-ion mechanism (Ascher–Vofsi reaction).[268,269] The same is true for the related sulphonylhalogenation based on the reaction between diazo compounds and SO_2.[270]

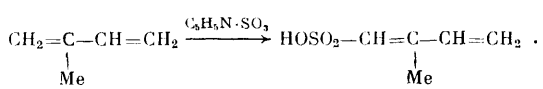
Sulfonylhalogenation by electrophilic addition in the absence of catalyst is rare. However, 1,4-addition does take place in the absence of catalyst by reaction of 1,3-butadiene, *trans*-piperylene, isoprene, and 2,3-dimethyl-1,3-butadiene with arenesulfonyl iodides.[271] The regioselectivity of the reaction with piperylene and isoprene is in accord with a mechanism involving electrophilic addition.



R = H, Me.

The amount of the lesser regioisomer, i.e. the 1,4-adduct, depends on the reaction conditions, but never exceeds 17%.

Direct sulfonylation of alkadienes with pyridine.SO_3 complex is of potential synthetic interest, but has not been greatly studied.[272] In all examples, replacement of hydrogen proceeds at the most nucleophilic carbon atom, being C_1 in the case of isoprene.



The mechanism of this reaction has not been studied. However, in all probability it is similar to aromatic electrophilic substitution. The authors of these investigations consider that reaction involves the intermediate formation of a 1 : 2 complex between the alkadiene and pyridine.SO_3.

VI. The addition of compounds with an electrophilic nitrogen atom

The addition of compounds with an electrophilic nitrogen atom to unsaturated compounds has not been studied extensively. The mechanism of such reactions has only been established in certain instances, but even here there is uncertainty in some respects. There is evidence to support electrophilic attack at the double bond by such reagents as nitrosyl chloride ($NO^{\delta+}Cl^{\delta-}$), N_2O_3, N_2O_4, nitryl halides ($NO_2^{\delta+}Hal^{\delta-}$), etc. However, one cannot exclude the possibility of addition of the reagents via a four-centred transition state, or by a free radical mechanism as a result of the weak polarisation.[2,273]

1. Addition of nitrogen oxides

NOCl adds to 1,3-butadiene at the 1,2-position in accordance with the Markovnikov rule, followed oxidation of the resulting nitroso compounds to nitro derivatives.[274] It is likely that this reaction proceeds through a four-centred transition state.[5]

Dinitro compounds and nitro(nitroso)alkenes are obtained by interaction of conjugated dienes with N_2O_3. Thus, 2,3-dimethyl-1,3-butadiene affords 2,3-dimethyl-1,4-dinitro-2-butene and 2,3-dimethyl-4-nitro-1-nitroso-2-butene dimer.[275,276]

1,3-Butadiene,[277,278] 2,3-dimethyl-1,3-butadiene,[279] 2,3-di-tert-butyl-1,3-butadiene[280] and 1,4-diphenyl-1,3-butadiene[281,282] yield 1,4-adducts with N_2O_4, while 2,3-diphenyl-1,3-butadiene[283] affords a mixture of 1,2- and 1,4-adducts.

The interaction of nitryl chloride with 1,3-butadiene, isoprene and piperylene in methylene chloride leads to a mixture of 1,4-adducts and products derived by isomerisation of the latter wherein the double bond migrates towards the nitro group.[284,285] Such isomerisation of unsaturated nitro compounds has been reported elsewhere in the literature.[286]

The addition of nitryl iodide ($N_2O_4 + I_2$) to 1,3-alkadienes leads to the formation of only 1,4-adducts.[287–289]

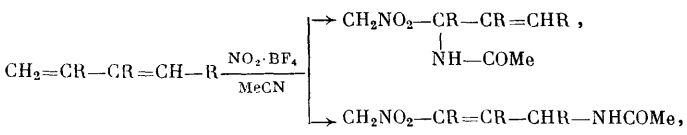
It is possible to nitrate 1,3-butadiene with concentrated nitric acid.[290,291] However, there are no details on this reaction, and it cannot be excluded that it proceeds with the participation of nitrogen oxides by a radical mechanism.

Recently, the reaction of 1,3-alkadienes with nitronium acetate [$HNO_3 + (MeCO)_2O$] was studied.[292] Thus, the reagent adds to isoprene to give a 3 : 7 mixture of 1,2- and 1,4-adducts, the latter containing 85% of the *trans*-isomer. In contrast to nitronium acetate, the corresponding trifluoroacetate (trifluoroacetic anhydride with added NH_4NO_3) adds to 1,3-alkadienes at the 1,2-position according to the Markovnikov rule.[293]

The adducts formed in the two reactions mentioned above readily eliminate acetic or trifluoroacetic acid to yield 1-nitro-1,3-alkadienes.

Nitronium fluoroborate has been used to prepare solvo-adducts.[294,295] In acetonitrile reaction with 1,3-alkadienes affords acetylaminonitro compounds. The ratio of 1,2- to 1,4-adducts is as follows: 48 : 51 for 1,3-butadiene, 39 : 50 for isoprene, 35 : 35 for

2,3-dimethyl-1,3-butadiene, 26:64 for piperylene, and 6:78 for 2,4-hexadiene.



R = H, Me.

Treatment of chloroprene with N_2O_4 leads to both 1,4- and 1,2-adduct, the former predominating.[296,297] The addition of NO_2Cl affords 1,4-adducts and products derived by their subsequent isomerisation (the double bond shifting towards the nitro group).

There are many reports on the nitration of polyhalogenated 1,3-alkadienes. Thus, nitration of 1,4-dichloro-1,3-butadiene with HNO_3 at 0–70 °C leads to *trans,trans*-1,4-dinitro-1,4-dichloro-1,3-butadiene, while treatment with $Cu(NO_3)_2$ at 20 °C leads to the formation of 1,4-dinitro-1-chloro-1,3-butadiene.[298]

The addition of N_2O_4 to polyhalogenated 1,3-butadienes proceeds mainly at the 1,4-position. Thus, a mixture of fluorinated 1,4-dinitro-2-butenes and 4-nitro-2-buten-1-ol nitrites was obtained on nitration of 1,1,4,4-tetrafluoro- and perfluoro-1,3-butadiene,[299] while the interaction of 1,2,3,4-tetrachloro-1,3-butadiene[89,300] and 1,1,2,4,4-pentachloro-1,3-butadiene[301] with N_2O_4 gives only 1,4-dinitro-adducts.

2. Reactions with aromatic diazo compounds

The reactions of 1,3-dienes with diazonium salts represent a special area of study. Recently, 1,4-halogenoarylation of 1,3-dienes in the presence of copper salts has been widely applied. Normally, reaction proceeds by a radical-ion mechanism,[302–305] but in certain cases an electrophilic mechanism is possible in the absence of copper ion.

1,3-Alkadienes participate in azo coupling with active diazonium salts in the same manner as aromatic compounds. The mechanism of this azo coupling has not been studied. However, one could invoke a mechanism similar to electrophilic aromatic azo coupling.

This reaction was discovered in 1919 by Meyer.[306] Terent'ev proposed an application of the method for the assay of 1,3-dienes in hydrocarbon mixtures.[307] It was studied more recently by Arbuzov and Rafikov, as exemplified by reactions with 1,3-butadiene and 2,4-hexadiene.[308] Brightly coloured crystalline azo compounds were isolated, and converted to the corresponding pyrazolines on reduction.

VII. Conclusion

From the data set out in this review, certain general conclusions can be drawn on electrophilic addition to 1,3-dienes.

The regioselectivity of electrophilic addition to 1,3-dienes is dependent on the nature of the electrophile, the structure and configuration of the 1,3-alkadiene, the nature of the solvent, the concentration of the reactants, and the temperature.

The reactions with hydrogen-containing electrophiles proceed with formation of carbenium ions, stabilised by allylic conjugation; in general, electrophilic attack takes place at the most nucleophilic atom of the conjugated system in accordance with the Markovnikov rule. The addition of HCl to 2-methyl-2,4-pentadiene is an exception: a tertiary carbenium ion, stabilised by hyperconjugation, is predominantly formed in this case.

Dilution favours electrophilic addition of halogens. Normally, the latter attack the terminal carbon atom of the conjugated system, but the nature of the halogen is an important factor. The position of attack by chlorine is determined by the electron density in the system, and evidently leads to that carbenium or ionium ion which is energetically most favoured. Attack by bromine and iodine need not take place at the most nucleophilic atom of the conjugated system since, being associated with formation of a cyclic onium salt, may be subject to steric factors.

The proportion of 1,2- and 1,4-adducts is determined first and foremost by the structure of the intermediate. The closer the intermediate is, in structure, to a carbenium ion, the more likely is 1,4-addition. Sulphenyl chlorides, which form stable episulphonium ions, add almost exclusively at the 1,2-position, in spite of the fact that such adducts tend to rearrange, even at room temperature, into the thermodynamically more stable 1,4-adducts.

The solvent has an effect on the regioselectivity of addition, either by virtue of its higher or lower polarity, or by its involvement in formation of the intermediate.

Both addition and replacement of hydrogen by halogen take place on treatment of 1,3-alkadienes with fluorine or chlorine.

1,3-Alkadienes participate in electrophilic substitution with nitronium salts, diazonium salts and pyridine.SO_3 complex, in the same manner as aromatic substrates.

Solvo-adducts may be formed on reaction of 1,3-alkadienes with halogens and with compounds containing electrophilic sulphur or nitrogen atoms; in the second stage of the addition process, a hydroxyl-containing nucleophile (e.g. water, alcohols, carboxylic acids, H_2O_2) or a nitrogen-containing nucleophile, such as a nitrile or a carboxylic acid amide, may participate.

The electrophilic addition to 1,3-alkadienylphosphonates is particularly interesting since, here, phosphorus-containing heterocyclics are formed as a result of intramolecular trapping of a nucleophilic centre.

All of these chemical properties of 1,3-alkadienes and their derivatives have been applied in organic synthesis, and the possibilities of broadening their synthetic value are by no means exhausted.

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