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1,3-DICHLOROBUT-2-ENE AND NEW PREPARATIONS BASED ON IT

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I. INTRODUCTION

Soon after its discovery, 1,3-dichlorobut-2-ene, one of the side-products of the manufacture of chloroprene rubber [1-5], attracted the attention of chemists who attempted to find applications for it. There are several reviews dealing with the reactions of 1,3-dichlorobut-2-ene and its applications [6-9], the last (published in 1954) covering only certain aspects of this problem. Since in recent years many papers have appeared, describing various interesting syntheses based on this compound, we have attempted an assessment of the importance of the investigations which have been made.

In the manufacture of chloroprene rubber 1,3-dichlorobut-2-ene is formed as a result of the addition of a second molecule of hydrogen chloride to vinylacetylene in the presence of a copper catalyst [1,2]:

$$HC\equiv C-CH=CH_2 \xrightarrow[CuCl]{HCl} [CH_2=C=CH-CH_2Cl] \rightarrow$$
$$\rightarrow CH_2=CCl-CH=CH_2 \xrightarrow[CuCl]{HCl} CH_2CCl=CH-CH_2Cl.$$

Under the usual conditions of chloroprene synthesis the yield of 1,3-dichlorobut-2-ene does not exceed 3%, but it can clearly be increased by using an excess of hydrochloric acid [2]. Carothers, who first described 1,3-dichlorobut-2-ene, quotes the following physical constants for this compound: b.p. 127-129°/756 mm and 53-54°/50 mm; d_4^{20} 1.1591; n_D^{20} 1.4724. [2] Distilled 1,3-dichlorobut-2-ene is a colourless liquid with a sharp smell and lachrymatory action.

Later it was found that the 1,3-dichlorobut-2-ene obtained by dehydrochlorination of monovinylacetylene consists of two stereosiomers (*cis* and *trans*). Hatch and coworkers separated the geometrical isomers of 1,3-dichlorobut-2-ene by fractional distillation and investigated their properties [10-13]. According to their data, the mobility of the allyl chlorine in the high-boiling β-isomer (b.p. 131°/748 mm) is higher than in the low-boiling α-isomer (b.p. 127.8°/745 mm), while the latter is higher than in allyl chloride [11-13]. Heating favours the conversion of the β-isomer to the α-isomer [10,11].

The configuration of the stereoisomers was convincingly demonstrated by reduction of the α and β forms with $LiAlH_4$ to the *trans*- and *cis*-2-chlorobut-2-enes respectively [13]:

$$ClCH_2-\underset{\|}{C}(Cl)-CH_3 \rightarrow CH_3-\underset{\|}{C}(Cl)-H \qquad H-\underset{\|}{C}(Cl)-CH_2Cl \rightarrow H-\underset{\|}{C}(Cl)-CH_3.$$

The high reactivity of 1,3-dichlorobut-2-ene depends primarily on the mobility of the allyl chlorine atom. Thus 1,3-dichlorobut-2-ene is readily hydrolysed and reacts with aromatic hydrocarbons, malonic and acetoacetic esters, ammonia and amines, sodium cyanide, thiocyanate salts, thiourea, etc.

The double bond in 1,3-dichlorobut-2-ene readily undergoes addition reactions and is ruptured by the action of oxidants. As was to be expected, the chlorine atom at the double bond cannot be substituted: both in 1,3-dichlorobut-2-ene itself and in its derivatives it can be removed as HCl by the action of alkali and sulphuric acid. In the first case an acetylenic compound or its isomerisation product is formed, and in the second a carbonyl compound (sulphuric acid hydrolysis):

$$-\underset{|}{C}(Cl)=\underset{|}{C}(H)- \rightarrow -\overset{\|}{C}(=O)-CH_2- + HCl.$$

Thus the possibilities of syntheses starting from 1,3-dichlorobut-2-ene are inexhaustable. The compounds formed (ethers, esters, amines, etc.) by the substitution of the

allyl chlorine atom with various groups can be of intrinsic interest and the compounds formed can serve as starting materials for the preparation of a wide variety of substances. Sulphuric acid hydrolysis, oxidation, and dehydrochlorination reactions have proved particularly fruitful. The present review deals with the main types of synthesis based on 1,3-dichlorobut-2-ene.

II. 3-CHLOROBUT-2-ENOL AND ITS ETHERS

The hydrolysis of 1,3-dichlorobut-2-ene to 3-chlorobut-2-enol in the presence of various alkaline reagents [Na_2SO_3, $NaHCO_3$, $Ca(OH)_2$] was first carried out by Klebanskii and Chevychalova[14]. The best yield of the chloro-alcohol is obtained with Na_2CO_3. This reaction was also studied in detail by Tishchenko[15]:

$$CH_3—CCl=CH—CH_2Cl \xrightarrow{H_2O} CH_3—CCl=CH—CH_2OH.$$

Akopyan and coworkers demonstrated that 3-chlorobut-2-enol is readily hydrogenated to butanol in the presence of Raney nickel[16]. Many workers showed that in the presence of CrO_3 3-chlorobut-2-enol is oxidised to β-chlorocrotonaldehyde[17,18], from which *trans*-β-chlorocrotonic acid[17] (catalytic oxidation), methylquinoline[18] (condensation with aniline), 4-methylpyridine[19] (condensation with guanidine), and other compounds were obtained.

3-Chlorobut-2-enol is dehydrochlorinated by alcoholic alkali to but-2-yn-1-ol,[12,17,20] which can be split by aqueous or powdered potassium hydroxide to yield methylacetylene[20]:

$$CH_3—C\equiv C—CH_2OH \xrightarrow{KOH} CH_3C\equiv CH+HCHO,$$

or oxidised by the chromic acid mixture to tetrolic acid (yield 35.8%)[17].

Sulphuric acid hydrolysis of 3-chlorobut-2-enol gives methyl vinyl ketone in 70% yield[21]:

$$CH_3CCl=CHCH_2OH \xrightarrow{16\%\ H_2SO_4} CH_3COCH=CH_2.$$

Ethers of 3-chlorobut-2-enol can be obtained both directly from 1,3-dichlorobut-2-ene and *via* the alcohol. 3-Chlorobut-2-enyl ethers of simple alcohols and phenols have been synthesised by the reaction of alkaline solutions of the latter with 1,3-dichlorobut-2-ene.[14,22-25] This reaction is quantitative and can be used for the determination of hydrolysable chlorine[26]. Mkryan showed that under the action of alcoholic alkali 3-chlorobut-2-enyl ethers split off HCl yielding acetylenic ethers[27], which are split by powdered potassium hydroxide into vinylacetylene and the corresponding alcohol or phenol[28]:

$$CH_3CCl=CH—CH_2Cl \xrightarrow[\text{alkali}]{ROH} CH_3CCl=CH—CH_2OR \xrightarrow[\text{alkali}]{}$$

$$\longrightarrow CH_3C\equiv C—CH_2OR \xrightarrow{KOH} CH_2=CH—C\equiv CH+ROH.$$

Isagulyants and Azizyan obtained many 3-chlorobut-2-enyl ethers of phenyls and alcohols and investigated their oxidation[29-32]. They showed that, like 1,3-dichlorobut-2-ene itself[33], the ethers are oxidised at the double bond in the presence of potassium permanganate and nitric acid. Oxidation of the 3-chlorobut-2-enyl ethers of phenols gave the corresponding aryloxyacetic acids:

$$ArOCH_2CH=CClCH_3 \xrightarrow{O_2} ArOCH_2COOH,$$

where Ar = phenyl, *m*-cresyl, *p*-t-butyl, *o*-methoxy-, *o*-ethoxy-, and *o*- and *p*-nitro-phenyl, 2,4-dinitrophenyl, and *m*- and *p*-phenylene.

Phenoxy- and 2,4-dichlorophenoxy-acetic acids and other compounds of this series are known to be herbicides and active stimulators and regulators of plant growth. The proposed method of synthesis of aryloxyacetic acid is superior to others known because the use of chloroacetic acid is eliminated. Compounds of the type of carboxymethylcellulose[34,35], whose value in various branches of industry is well known, were obtained similarly by oxidation of 3-chlorobut-2-enyl ethers of cellulose[34,36].

Durgaryan and Titanyan showed that oxidation with perbenzoic acid of aryloxychlorobutenes, as well as other compounds containing the 3-chlorobut-2-enyl group, results in the formation of epoxybutanes[37]:

$$ROCH_2CH=CClCH_3 \xrightarrow{O} ROCH_2CH—CClCH_3,$$

where R = alkyl or phenyl.

Vartanyan and Tosunyan proposed a new method of synthesis of high-boiling solvents such as butyl ether, butyl cellosolve, dibutylcellosolve, butylcarbitol, and others, consisting in catalytic reduction (Ni, Pt) of the corresponding 3-chlorobut-2-enyl ethers under a pressure of 25 atm[38,39]:

$$CH_3CCl=CHCH_2Cl \xrightarrow[\text{alkali}]{ROH} CH_3CCl=CHCH_2OR \xrightarrow[Ni/Pt]{H_2} CH_3CH_2CH_2CH_2OR,$$

where

$$R=CH_3CH_2CH_2CH_2—,\ HOCH_2CH_2—,\ CH_3CH_2CH_2CH_2OCH_2CH_2—,\ HOCH_2CH_2OCH_2CH_2—.$$

Thus butanol can be replaced by 1,3-dichlorobut-2-ene in the synthesis of many valuable solvents.

By cyanoethylation of 3-chlorobut-2-enol the same workers obtained 2-cyanoethyl 3-chlorobut-2-enyl ether, whose hydrolysis gave the corresponding acid[40].

$$CH_3CCl=CHCH_2OH + CH_2=CHCN \xrightarrow{KOH} CH_3CCl=CHCH_2OCH_2CH_2CN.$$

Many alkoxymethyl 3-chlorobut-2-enyl ethers have been obtained in good yields (60–90%) by the reaction of 3-chlorobut-2-enol with various chloromethyl ethers[41]:

$$CH_3CCl=CHCH_2OH + ClCH_2OR \rightarrow CH_3CCl=CHCH_2OCH_2OR,$$

where R = H or isoalkyl (C_1–C_5).

III. 3-CHLOROBUT-2-ENYL ESTERS OF CARBOXYLIC ACIDS

Esterification of carboxylic acids with 3-chlorobut-2-enol was first investigated by Petrov[42]. In his search for herbicidal preparations, Dovlatyan synthesised the 3-chlorobut-2-enyl esters[43-48] and amides[48] of many carboxylic acids. The esters were synthesised in good yields both by esterification of the carboxylic acids with 3-chlorobut-2-enol and by the reaction of the carboxylic acid salts with 1,3-dichlorobut-2-ene in the presence of catalytic amounts of pyridine and other bases:

$$\left.\begin{matrix} RCOOH + CH_3CCl=CHCH_2OH \\ RCOOM + CH_3CCl=CHCH_2Cl \end{matrix}\right\} \rightarrow RCOOCH_2CH=CClCH_3,$$

where R = aryloxy, 1- and 2-naphthoxy, alkyl, chloromethyl, and trichloromethyl.

Among the esters synthesised, particular interest attaches to the 3-chlorobut-2-enyl ester of 2,4-dichlorophenoxyacetic acid (crotilin)[43,47]; herbicidal properties are

not inferior to those of the highly active butyl ester[49], whose preparation requires butanol. Crotilin has been successfully tested under field conditions in various agricultural regions of the USSR.[49-51] 3-Chlorobut-2-enyl 4-chloro- and 2-methyl-4-chloro-phenoxyacetates exhibit high herbicidal activity against broad-leaved weeds whilst 3-chlorobut-2-enyl trichloroacetate is active against gramineous weeds[44]. The 3-chlorobut-2-enyl-substituted amides of the same carboxylic acids, obtained in best yields by the reaction of 3-chlorobut-2-enylamine (see the section on amines) with the free acids, are unexpectedly without high herbicidal activity[48].

Gefter synthesised the 3-chlorobut-2-enyl esters of adipic, sebacic, thiodipropionic, and phthalic acids by reaction of these acids (the anhydride in the case of the phthalic acid) with 3-chlorobut-2-enol in the presence of *p*-toluenesulphonic acid[52].

Vartanyan and coworkers obtained bis(3-chlorobut-2-enyl) phthalate in a higher yield (70 instead of 50%) by the reaction of sodium phthalate with 1,3-dichlorobut-2-ene in the presence of catalytic amounts of pyridine[53]. The ester was isolated as a mixture of two stereoisomers (liquid and crystalline). Tests on the individual isomers and their mixtures showed that as plasticisers they are not inferior to dibutyl phthalate. Mixtures of phthalate esters and 3-chlorobut-2-enyl salicylate can also be of interest as plasticisers[53]. The possible use of 3-chlorobut-2-enyl esters of carboxylic acids as plasticisers is being intensely studied at present[54].

IV. CONDENSATION WITH AROMATIC HYDROCARBONS AND RELATED REACTIONS

Isagulyants and Mushegyan showed that 1,3-dichlorobut-2-ene readily reacts with aromatic hydrocarbons in the presence of $AlCl_3$ with the formation of 1-aryl-3-chlorobut-2-enes[55-58]:

$$CH_3CCl{=}CHCH_2Cl + ArH \rightarrow CH_3CCl{=}CHCH_2Ar,$$

where Ar = phenyl, *p*-tolyl, *p*-cumenyl, and 1-naphthyl. This reaction was carried out by other workers in the presence of metallic aluminium[59] and anhydrous $ZnCl_2$.[60] The product of the condensation of naphthalene with 1,3-dichlorobut-2-ene in the presence of $ZnCl_2$ has been suggested as a rubber plasticiser[61,62].

1-Aryl-3-chlorobut-2-enes have been used in various reactions. The corresponding ketones were obtained by the action of concentrated sulphuric acid[57]:

$$CH_3CCl{=}CHCH_2Ar \xrightarrow{H_2SO_4} CH_3COCH_2CH_2Ar.$$

Reaction of 1-aryl-3-chlorobut-2-enes with sodium ethoxide yields 1-arylbut-2-ynes and 1-aryl-3-ethoxybut-1-enes.[57] The formation of the latter can be explained by an alkali-catalysed 1,3-hydride shift placing the double bond in conjugation with the aromatic system:

$$CH_3CCl{=}CHCH_2Ar \xrightarrow{C_2H_5ONa} \left[CH_3CClCH{=}CHAr\right] \rightarrow CH_3CHCH{=}CHAr.$$

When powdered potassium hydroxide in an inert solvent (benzene, toluene) is allowed to act on 1-aryl-3-chlorobut-2-enes, the latter undergo a similar reaction. The final products are 1-arylbuta-1,3-dienes and their dimers[63-67].

$$CH_3CCl{=}CH{-}CH_2Ar \xrightarrow{KOH} CH_2{=}CH{-}CH{=}CHAr,$$

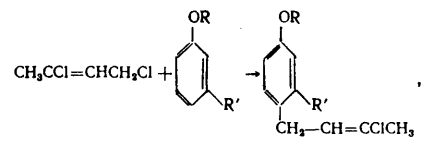
where Ar = phenyl, *p*-tolyl, *p*-cumenyl, 1-naphthyl, and *p*-phenoxyphenyl.

Oxidation of 1-aryl-3-chlorobut-2-ene with potassium permanganate yields the corresponding arylcarboxylic acids[56,58]. The reaction with perbenzoic acid gives substituted epoxybutanes as in the case of alkoxyphenoxy-3-chlorobut-2-enes and 1,3-dichlorobut-2-ene:[37]

$$CH_3CCl{=}CHCH_2Ar \xrightarrow{O} CH_3CCl{-}CHCH_2Ar.$$

2-Aminothiazole derivatives have been synthesised from the epoxybutanes by the action of thiourea[68].

Isagulyants and Azizyan showed that phenols and their ethers can also be reacted with 1,3-dichlorobut-2-ene in the presence of $AlCl_3$ giving 3-chlorobut-2-enyl derivatives[69]:



where R = H or C_2H_5 and R′ = H or CH_3. Condensation of *p*-(3-chlorobut-2-enyl)phenol with formaldehyde results in the formation of a transparent resin similar to the "100% resins".[69] In the presence of metal chlorides 1,3-dichlorobut-2-ene polymerises into film-forming substances[70]. Klebanskii *et al.*[71] investigated this reaction in detail and isolated both low-molecular-weight and high-molecular-weight polymerisation products, whose formation can be represented as follows:

$$CH_3CCl{=}CHCH_2Cl + FeCl_4^- \cdot {}^+CH_2CH{=}CClCH_3 \rightarrow$$

$$\rightarrow \left[CH_3CCl{=}HCCH_2{-}\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}{-}\overset{+}{C}ClCH_3 \cdot FeCl_4^-\right] \rightarrow CH_3CCl_2CHCH_2CH{=}CClCH_3 + FeCl_3. \quad \text{etc.}$$

When 1,3-dichlorobut-2-ene reacts under similar conditions with chloroprene[72], isoprene, or buta-1,3-diene[73], low-molecular-weight and high-molecular-weight compounds, probably telomerisation products, are also formed:

$$CH_3CCl{=}CHCH_2Cl + nCH_2{=}CXCH{=}CH_2 \rightarrow CH_3CCl{=}CHCH_2(CH_2CX{=}CHCH_2)_nCl,$$

where X = H. Cl, or CH_3.

V. REACTIONS WITH ORGANOMETALLIC COMPOUNDS

Reaction of 1,3-dichlorobut-2-ene with alkylmagnesium halides yields the corresponding substituted alkene[74-79]:

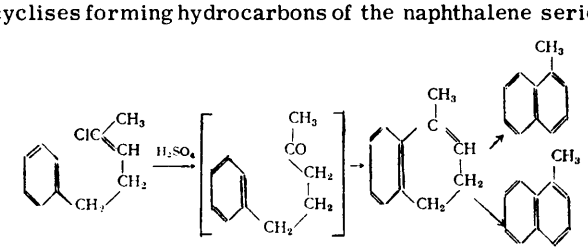
$$CH_3CCl{=}CHCH_2Cl + RMgX \rightarrow CH_3CCl{=}CHCH_2R + MgXCl,$$

where R = alkyl, aryl, or benzyl.

Like arylchlorobutenes, alkylchlorobutenes form the corresponding ketones under the action of sulphuric acid[41]:

$$CH_3CCl{=}CHCH_2R \xrightarrow{H_2SO_4} CH_3COCH_2CH_2R.$$

When R = benzyl, the intermediate carbonyl compound cyclises forming hydrocarbons of the naphthalene series[74-75]:

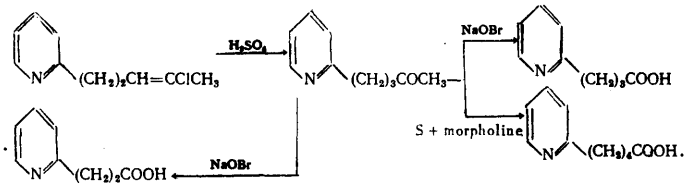


One of the communications from the Du Pont de Nemours Company[80] indicates the possibility of obtaining 2,7-dichloroocta-2,6-diene by allowing 1,3-dichlorobut-2-ene to react with metallic magnesium:

$$2CH_3CCl{=}CHCH_2Cl + Mg \rightarrow CH_3CCl{=}CH{\cdot}CH_2CH_2{\cdot}CH{=}CCl{\cdot}CH_3.$$

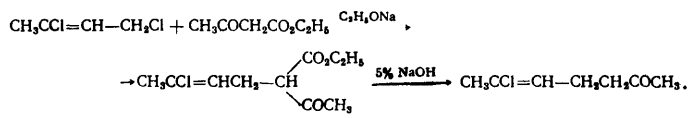
This compound was also prepared by Klebanskii and Vosik by the reaction of metallic magnesium with 1-iodo-3-chlorobut-2-ene synthesised by the action of potassium iodide on 1,3-dichlorobut-2-ene.[81]

The product of the reaction of 1,3-dichlorobut-2-ene with the sodium derivative of picoline can serve as the starting material for the preparation of a number of pyridyl derivatives of aliphatic acids[82]:

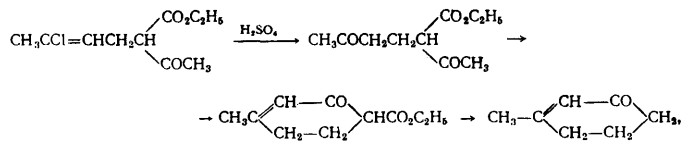


VI. SYNTHESES BASED ON THE PRODUCTS OF CONDENSATION OF 1,3-DICHLOROBUT-2-ENE WITH MALONIC AND ACETOACETIC ESTERS

As was to be expected, 1,3-dichlorobut-2-ene reacts particularly easily with acetoacetic ester, malonic ester, and other compounds containing an active methylene group. Wichterle and coworkers[83,84] and, independently, Isagulyants[85] obtained 3-chlorobut-2-enylacetoacetic ester whose ketone hydrolysis yielded 2-chlorohept-2-en-6-one:



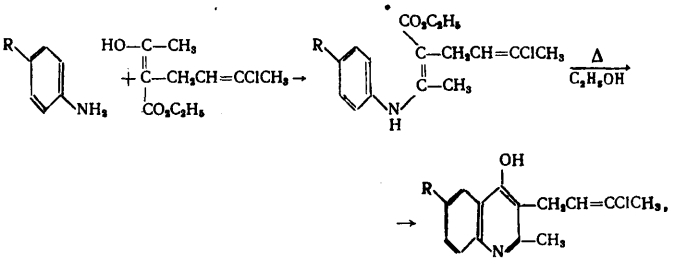
It has been shown that both the mono- and di-(3-chlorobut-2-enyl) derivatives of acetoacetic ester undergo sulphuric acid hydrolysis followed by cyclisation. The first derivative yields the ester of 4-methyl-2-oxocyclohex-3-en-1-carboxylic acid and a product of its ketone hydrolysis-1-methylcyclohex-1-en-3-one[83,84],



and the second derivative gives the di(3-oxobutyl)acetoacetic ester and the products of its subsequent cyclisation whose structure has not been reliably established[84-86].

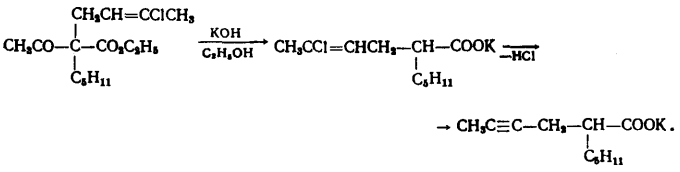
1-Methylcyclohex-1-en-3-one and its 5-alkyl derivatives were synthesised independently by Tatevosyan and coworkers[87-90], both by the same method as above and *via* the chloroheptenone. In particular, they obtained 5-isopropyl-1-methylcyclohex-1-en-3-one[89] (*d,l*-piperitone), which is used in the manufacture of terpenes.

Gyul'budagyan and coworkers obtained derivatives of 3-(3'-chlorobut-2'-enyl)-4-hydroxy-2-methylquinoline by the reaction of (3-chlorobut-2-enyl)acetoacetic ester with substituted anilines[91-93]:



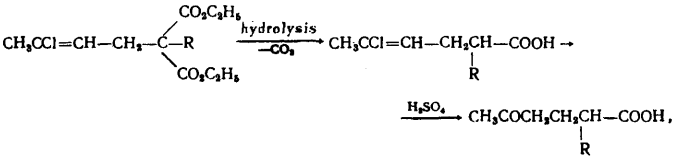
where R = H, alkyl, alkoxy, or CH_3CONH.

(3-Chlorobut-2-enyl)acetoacetic esters are convenient starting materials for the preparation of carboxylic acids of various structures. Thus acid hydrolysis of (3-chlorobut-2-enyl)isopentylacetoacetic ester followed by dehydrochlorination yields 2-(but-2'-ynyl)heptanoic acid[94]:



Acid hydrolysis of carboxymethyl-(3-chlorobut-2-enyl)-acetoacetic ester gave (3-chlorobut-2-enyl)succinic acid and its esters[95].

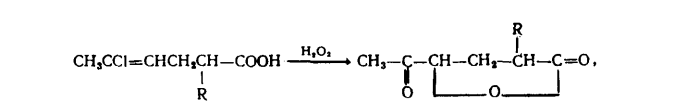
Tatevosyan and coworkers[96], and, independently, Wichterle[97] obtained 5-chlorohex-4-enoic acid by the hydrolysis of (3-chlorobut-2-enyl)malonic ester, sulphuric acid hydrolysis of the former yielding a keto-acid; this reaction was extended to alkyl-[98,99] and phenyl-(3-chlorobut-2-enyl)-malonic[100] esters:



where R = H, alkyl, or phenyl.

The chlorohexenoic and acetylbutyric acids obtained in this way can in turn be used as starting materials for various other syntheses. Thus 2-ethylhex-4-ynoic acid was obtained by the action of alcoholic potassium hydroxide on 5-chloro-2-ethylhex-4-enoic acid[98].

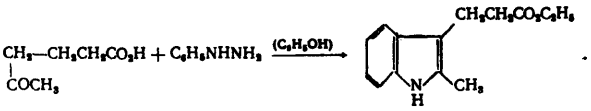
Dangyan and coworkers showed that the oxidation of the chlorohexenoic acid and its 2-substituted derivatives by hydrogen peroxide in formic or acetic acid yields δ-oxo-γ-lactones and therefore constitutes a convenient method for the synthesis of the latter[101-103]:



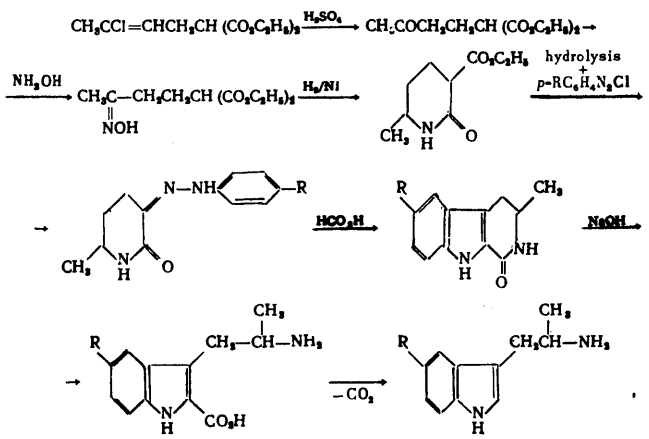
where R = H, alkyl, cyclohexyl, phenyl, benzyl.

γ-Acetylbutyric acid[104] and its α-substituted derivatives[105] readily condense with phenylhydrazine with the formation of esters of β-(2-methylindol-3-yl)propionic acid

which gave the corresponding hydrazides, indolylmercaptooxadiazoles[105], and indolylpropylamines[106] and their *N*-dialkyl derivatives[107]:

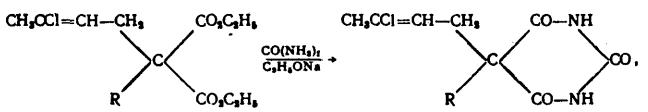


Other derivatives of indole, homologues of tryptamine and 5-methoxytryptamine with an α-methyl group in the ethylamine side chain, which are of special interest as biologically active substances (inhibitors of monoamine-oxidase)[108,109], have been synthesised from (3-chlorobut-2-enyl)malonic ester[109]:



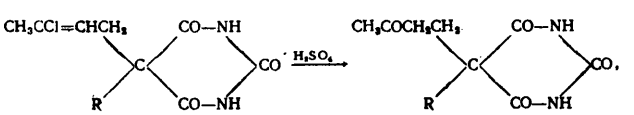
where R = H or OCH_3.

5-Alkyl-5-(3′-chlorobut-2′-enyl)- and 5,5-di(3′-chlorobut-2′-enyl)-barbituric acids have been synthesised by Tatevosyan and coworkers[110,111] and also by Wichterle and Němeček[112] by the reaction of urea with the corresponding malonic ester:



where R = alkyl or 3-chlorobut-2-enyl.

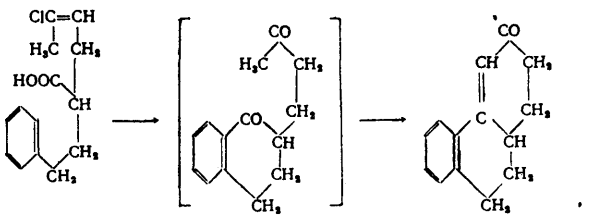
Contrary to expectation, these compounds had no soporific properties and proved to be toxic for animals[111]. The same applies to 5-ethyl-5-(3′-chlorobut-2′-enyl)thiobarbituric acid which was synthesised in a similar way[113,114]. Sulphuric acid hydrolysis of 3′-chlorobut-2′-enyl- and alkyl-(3′-chlorobut-2′-enyl)-barbituric acids gave the corresponding keto-derivatives[115]:



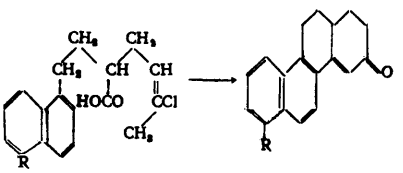
where R = H, alkyl, or cyclohexyl.

Tatevosyan and coworkers have made extensive studies on the synthesis of polycyclic hydroaromatic ketones, based on the sulphuric acid hydrolysis and subsequent double cyclisation of 3-chlorobut-2-enylarylalkanecarboxylic acids obtained from the corresponding arylalkyl-(3-chlorobut-2-enyl)malonic esters. The hydroaromatic ketones are used as starting materials for the synthesis of physiologically active compounds, in particular carcinogens, other known methods for the preparation of which are as a rule difficult.

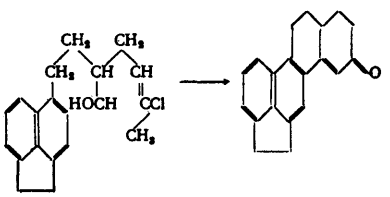
3-Oxo-1,2,3,9,10,10a-hexahydrophenanthrene was obtained in 75% yield by the action of sulphuric acid on α-(3-chlorobut-2-enyl)-γ-phenylbutyric acid[116]:



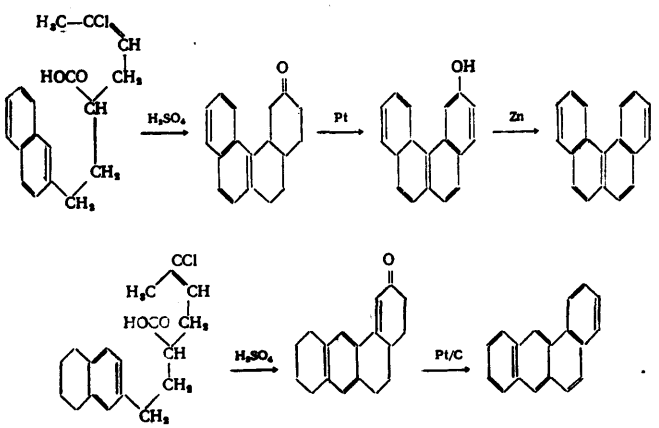
7-Methyl-,[117] 6-methyl-,[118] 6- and 7-methoxy-,[119] and 8-methyl- and 8-methoxy-3-oxo-1,2,3,9,10,10a-hexahydrophenanthrenes[120] were synthesised similarly. Ketones of the chrysene series were obtained by the action of sulphuric acid on α-(3-chlorobut-2-enyl)-γ-(1-naphthyl)-,[121] α-(3-chlorobut-2-enyl)-γ-(5-methoxynaphthyl)-,[122] and α-(3-chlorobut-2-enyl)-γ-(acenaphthyl)-butyric acids[123]:



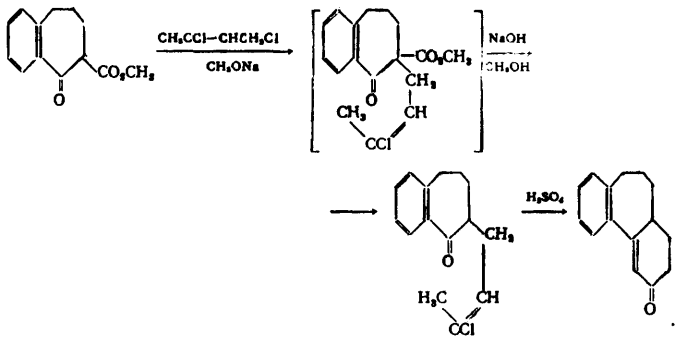
where R = H or OCH_3.



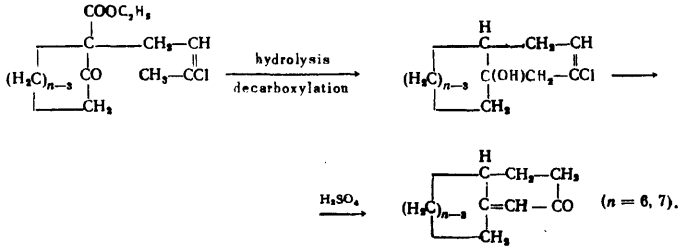
On reaction with sulphuric acid α-(3-chlorobut-2-enyl)-γ-(2-naphthyl)butyric acid yields ketones of the 3,4-benzophenanthrene series[124], while the 5,6,7,8-tetrahydronaphthyl derivatives give the ketones of the 1,2-benzophenanthrene series[125]. The corresponding benzophenanthrenes can be obtained by the dehydrogenation of these ketones:



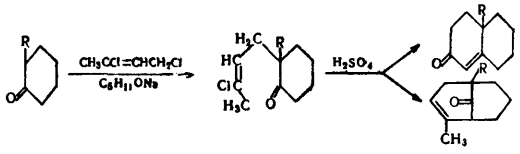
2-Oxo-2,3,4,4a,6,7-hexahydro-5*H*-dibenzo[*a*,*c*]cycloheptatriene can be synthesised by two-stage cyclisation of α-(3-chlorobut-2-enyl)-δ-phenylvaleric acid. However, it is obtained in best yield from benzosuberone [126]:



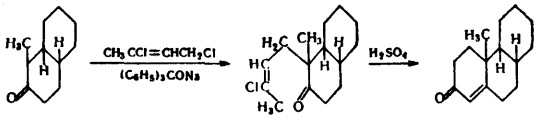
A similar cyclisation was carried out by Prelog *et al.* in the case of 2-(3′-chlorobut-2′-enyl)-2-ethoxycarbonylcyclic ketones [127]:



Julia studied the synthesis of some keto-derivatives of bicyclo[1,3,3]-nonene and hexahydronaphthalene from the products of the condensation of 1,3-dichlorobut-2-ene with cyclohexanone, 2-methylcyclohexanone, and isophorone [128–130]:



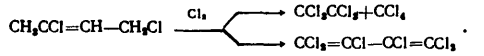
A similar cyclisation was achieved by Pinder and Robinson starting from the products of the condensation of 1,3-dichlorobut-2-ene with 1-methyl-*cis*-2-decalone [131]:



VII. SYNTHESIS OF CHLORINATED HYDROCARBONS

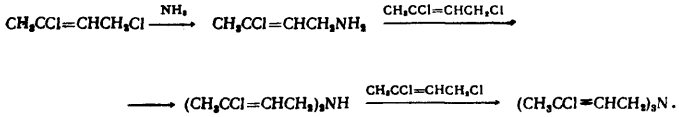
Carothers and coworkers showed that chlorination of 1,3-dichlorobut-2-ene in carbon tetrachloride and in the absence of solvent results in a complex mixture of chloro-derivatives [132,133]. At 40–60° the main product of the reaction is 1,2,3,3-tetrachlorobutane and at low temperatures 1,2,3-trichlorobut-3-ene and 1,2,3,3,4-pentachlorobutane. On dehydrochlorination of 1,2,3-trichlorobut-3-ene in the presence of alcoholic potassium hydroxide, 2,3-dichlorobuta-1,3-diene is formed while dehydrochlorination of 1,2,2,3,4-pentachlorobutane yields 1,2,3-trichlorobuta-1,3-diene [134,135], which on copolymerisation with chloroprene gives rubberlike products [135]. Klebanskii and coworkers made a detailed study of the above reactions and established the optimum conditions for the preparation of both chlorination and dehydrochlorination products [136].

Chlorination of 1,3-dichlorobut-2-ene at a high temperature (400–500°) in the presence of activated carbon yields carbon tetrachloride and hexachloroethane [137], whereas in the absence of catalyst hexachlorobuta-1,3-diene is formed [138]. The last compound has been proposed as an anti-phylloxera agent:



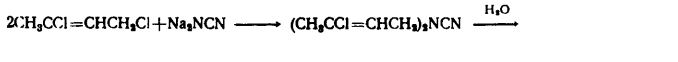
VIII. SYNTHESIS OF NITROGEN-CONTAINING COMPOUNDS

Wichterle and Hudlický showed that reaction of 1,3-dichlorobut-2-ene with aqueous ammonia (even in the presence of a large excess of the latter) yields predominantly the tertiary amine, whereas in liquid ammonia the primary and secondary amines are formed [139]:



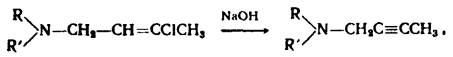
Babayan and Grigoryan synthesised these amines in ethanol and showed that the principal reaction product can be the primary, secondary, or tertiary amine depending on the conditions (temperature, excess of ammonia) [140]. Japanese workers have described a similar method of preparing 3-chlorobut-2-enylamines [141].

The secondary amine can be obtained by the hydrolysis of the product of condensation of 1,3-dichlorobut-2-ene with sodium cyanamide [142]:



The hydrogen atoms in primary and secondary amines [139–141, 143–152], in amides [139,153,154], imides [155], and sulphonamides [156] are just as easily substituted.

Dehydrochlorination of 3-chlorobut-2-enylamines was studied by Babayan and coworkers, who established that dialkyl- [144,157] and diaryl-3-chlorobut-2-enyl amines [149], as well as di- and tri-(3-chlorobut-2-enyl)amines [149], give the corresponding acetylenic amines when acted upon by alkali:



where

R=H, R′=$CH_3CH=CCl-CH_3$ (91.8%);
R=R′=$CH_3CH=CCl-CH_3$ (89.6%); R=R′=C_6H_5 (62.15%).

Under the action of metallic sodium these compounds are very readily isomerised to but-1-ynylamines, but-2-enylamines being formed at the same time [158]:



A very convenient method of synthesising acetylenic amines was proposed on the basis of these data [157]:

$$R_2NCH_2CH{=}CClCH_3 \xrightarrow{NaOH} R_2NCH_2C{\equiv}C{-}CH_3 \xrightarrow{Na} \longrightarrow R_2NCH_2CH_2C{\equiv}CNa \xrightarrow{CH_3I} R_2NCH_2CH_2C{\equiv}C{-}CH_3, \text{ etc.}$$

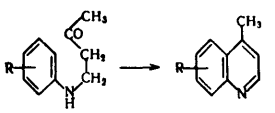
Dialkylbut-1-ynyl- and dialkylbut-2-enyl-amines are very convenient raw materials for the synthesis of various halogenated dialkylamino-derivatives of butane and butene [159,160].

3-Chlorobut-2-enylamine [139] and other amines containing only one 3-chlorobut-2-enyl group [144,145,161] form the corresponding aminobutanones when acted upon by concentrated sulphuric acid:

$$CH_3CCl{=}CHCH_2NRR' \xrightarrow{H_2SO_4} CH_3COCH_2CH_2NRR',$$

where R, R' = H, alkyl, or aryl.

Vavrečka [143] and, independently, Babayan and coworkers [161,162] showed that in the presence of $FeCl_3$ and other catalysts arylaminobutanones readily cyclise into lepidines:



The lepidines can also be obtained under conditions in which butynylamines are hydrated [146,163].

According to the data of Wichterle and Hudlický, amines and amides containing two [139] and three [164] 3-chlorobut-2-enyl groups are cyclised under conditions of sulphuric acid hydrolysis, di-(3-chlorobut-2-enyl)amines and the corresponding amides of carboxylic and sulphonic acids being converted into tetrahydropyridine derivatives:

$$RN(CH_2CH{=}CClCH_3)_2 \xrightarrow{H_2SO_4} \left[RN(CH_2CH_2COCH_3)_2\right] \longrightarrow RN\begin{array}{l}CH_2{-}CH_2\\ CH_2{-}C{=}C{-}CH_3\\ \qquad\quad |\\ \qquad\quad COCH_3\end{array},$$

where R = H, alkyl, acyl, benzyl, or *p*-toluenesulphonyl.

Tri-(3-chlorobut-2-enyl)amine forms a bicyclic compound under these conditions.

With 3-chloro-1-dimethylaminobut-2-one as an example, it has been shown that 3-chlorobut-2-enylamines are readily chlorinated in hydrochloric acid solution forming trichloro-derivatives, which by dehydrochlorination and further chlorination can be converted into di- and tetra-chloro-derivatives [165]:

$$(CH_3)_2NCH_2CH{=}CClCH_3 \xrightarrow[HCl]{Cl_2} (CH_3)_2NCH_2CHClCCl_2CH_3 \xrightarrow{KOH} \longrightarrow (CH_3)_2NCH_2CCl{=}CClCH_3 \xrightarrow[HCl]{Cl_2} (CH_3)_2NCH_2CCl_2CCl_2CH_3.$$

Among other reactions of 3-chlorobut-2-enyl derivatives that of (3'-chlorobut-2'-enyl)-2,5-dimethylpiperidin-4-ol with benzoyl chloride is of interest [166], since the resulting benzoate, like other compounds of this series [151], may possess anaesthetic properties.

Babayan and coworkers have made extensive studies on quaternary ammonium compounds, in particular those with a 3-chlorobut-2-enyl group. They established from reactions of many compounds that quarternary salts containing 3-chlorobut-2-enyl or butynyl groups are readily split on heating with aqueous alkali into dienes (enynes) and the tertiary amine [167,168]:

$$R_3\overset{+}{N}\,\underset{Cl^-}{}\,CH_2CH{=}CClCH_3 + NaOH \xrightarrow[80-90^\circ]{H_2O} R_3N + CH_2{=}CH{-}C{\equiv}CH + CH_2{=}CCl{-}CH{=}CH_2.$$

This reaction constitutes a convenient method for the preparation of dienes and enynes on the one hand and tertiary amines on the other. The dehydrochlorination of quaternary ammonium salts containing a 3-chlorobut-2-enyl group can be achieved by the action of alkali at a lower temperature [168] and takes place much more readily than in the case of the tertiary amines [144].

Thermal degradation of ammonium salts containing a 3-chlorobut-2-enyl group results in the formation of chloroprene as well as 1,3-dichlorobut-2-ene [169,170]:

$$R_3\overset{+}{N}\,\underset{Cl^-}{}\,CH_2CH{=}CClCH_3 \longrightarrow \begin{cases} R_3N + HCl + CH_2{=}CCl{-}CH{=}CH_2 \\ R_3N + CH_2CCl{=}CHCH_2Cl \end{cases}$$

The first reaction is similar to the splitting of quaternary ammonium salts by alkali and can be used for the preparation of both the diene and tertiary amines.

Primary and secondary amines can be readily alkylated by quaternary ammonium salts containing a 3-chlorobut-2-enyl group [145] or even by 1,3-dichlorobut-2-ene itself in the presence of catalytic quantities of the quaternary ammonium salts [171] (*N*-alkylation). Other compounds containing a mobile hydrogen atom are alkylated similarly: acetoacetic ester, malonic ester, phenylacetylene, acetylacetone [172], bis(diphenylsulphonyl)methane [173] (*C*-alkylation), phenols and alcohols [173-175] (*O*-alkylation), and mercaptans and thiophenols [173] (*S*-alkylation).

In the reaction of di-(3-chlorobut-2-enyl)dimethylammonium chloride with tertiary amines containing an *N*-methyl group, the latter is exchanged for a 3-chlorobut-2-enyl group [176]. This transalkylation reaction makes it possible to replace secondary amines, in the synthesis of tertiary amines, by the more readily available tertiary amines (for example methylaniline can be replaced by dimethylaniline).

Among other nitrogen-containing compounds obtained from 1,3-dichlorobut-2-ene, 3-chlorobut-2-enyl cyanide is of interest. The first description of its preparation by the reaction of 1,3-dichlorobut-2-ene with sodium cyanide and its hydrolysis to the corresponding amide is given in a brief communication by Azatyan and Arakelyan [177]:

$$CH_3CCl{=}CHCH_2Cl \xrightarrow{NaCN} CH_3CCl{=}CHCH_2CN \longrightarrow CH_3CCl{=}CHCH_2CH_2NH_2.$$

Vartanyan showed that alcoholysis of 3-chlorobut-2-enyl cyanide with ethanol in the presence of sulphuric acid followed by sulphuric acid hydrolysis of the resulting chloropentenoate ester yields the corresponding ester of levulinic acid [178]. Hydrolysis of the nitrile with hydrochloric acid gives a number of levulinate esters in good yields [179]:

$$CH_3CCl{=}CHCH_2CN \xrightarrow[HCl]{ROH} CH_3CCl{=}CHCH_2{-}C(=O){-}OR \xrightarrow{H_2SO_4} CH_3COCH_2CH_2C(=O){-}OR',$$

where R = CH_3, C_2H_5, C_3H_7, C_4H_9, iso-C_4H_9, or iso-C_5H_{11}. Fetizon and Julia obtained levulinic acid in a similar way — by sulphuric acid hydrolysis of the chloropentenoic acid [180].

IX. DEHYDROCHLORINATION OF 1,3-DICHLOROBUT-2--ENE

The dehydrochlorination of 1,3-dichlorobut-2-ene was studied particularly thoroughly, since the aim was to recover and return to the manufacturing process the main reaction product — chloroprene or even the initial vinylacetylene.

The first investigations on these lines were carried out by Klebanskii and coworkers [14,181], who showed that 1,3-dichlorobut-2-ene is dehydrochlorinated to chloroprene in satisfactory yield by fused potassium hydroxide and by being passed over a copper catalyst at 250–300° (or better at 350–400°) in the presence of water vapour [181]:

$$ClCH_2{-}CH{=}CCl{-}CH_3 \xrightarrow{-HCl} CH_2{=}CCl{-}CH{=}CH_2.$$

There are indications that the dehydrochlorination can be carried out at a higher temperature (530°) in the absence of catalyst [182].

The dehydrochlorination of 1,3-dichlorobut-2-ene in the presence of potassium hydroxide in ethylene glycol has been proposed as a laboratory method for the preparation of vinylacetylene (50% yield) [183]:

$$ClCH_2{-}CH{=}CCl{-}CH_3 \xrightarrow[-2HCl]{} CH_2{=}CH{-}C{\equiv}CH.$$

As mentioned above, Babayan and coworkers showed that, in the alkaline [167,168] and thermal [169,170] degradation of quaternary salts containing a 3-chlorobut-2-enyl group, chloroprene and vinylacetylene are formed together with the tertiary amine.

X. SYNTHESIS OF SULPHUR-CONTAINING COMPOUNDS

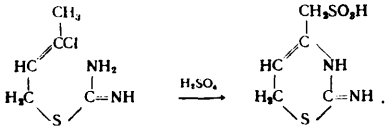
Products of the condensation of alkyl halides with thiourea — *S*-substituted isothioureas (thiuronium salts) — are convenient starting materials for the preparation of various organosulphur compounds. The product of the condensation of 1,3-dichlorobut-2-ene with thiourea — *S*-(3--chlorobut-2-enyl)isothiourea hydrochloride — was described for the first time by Procházka and Wichterle [184] and, independently, by Esayan and Sarkisyan [185]:

$$CH_3CCl{=}CHCH_2Cl + SC(NH_2)_2 \longrightarrow CH_3CCl{=}CHCH_2S{-}C(=NH)NH_2 \cdot HCl.$$

Recently, it has been shown that this compound is an active defoliant desiccant of the cotton plant [186]. Its hydrolysis gave 3-chlorobut-2-enethiol [184], which can be obtained directly from 1,3-dichlorobut-2-ene by its reaction with sodium hydrosulphide [184,187]:

$$CH_3CCl{=}CHCH_2S{-}C(=NH)NH_2 \cdot HCl \xrightarrow{H_2O(NaOH)} CH_3CCl{=}CHCH_2SH.$$
$$CH_3CCl{=}CHCH_2Cl \xrightarrow[NaHS]{}$$

When *S*-(3-chlorobut-2-enyl)isothiourea is subjected to sulphuric acid hydrolysis, a crystalline product is formed [184,188]:



Chlorination of the *S*-thiourea derivatives in an aqueous medium yields 3-chlorobut-2-enesulphonyl chloride, whose hydrolysis in an alkaline medium gives the 3-chlorobut-2--enesulphonate [185].

$$CH_3CCl{-}CHCH_2S{-}C(=NH)NH_2 \cdot HCl \xrightarrow{Cl_2+H_2O} CH_3CCl{=}CHCH_2SO_2Cl \xrightarrow[H_2O]{NaOH} CH_3CCl{=}CH.$$

The last compound is obtained in a better yield by the reaction of 1,3-dichlorobut-2-ene with SO_2 in an alkaline medium. The resulting mixture of *cis*- and *trans*-stereoisomers was separated by fractional crystallisation [189]. A keto-sulphonic acid is formed on sulphuric acid hydrolysis of this compound [189,190]:

$$CH_3CCl{=}CHCH_2SO_3Na \xrightarrow{H_2SO_4} CH_3COCH_2CH_2SO_3H.$$

Under the same conditions 3-chlorobut-2-enesulphonyl chloride splits into methyl vinyl ketone, SO_2, and HCl: [190]

$$CH_3CCl{=}CHCH_2SO_2Cl \xrightarrow{H_2SO_4} [CH_3COCH_2CH_2SO_2Cl] \longrightarrow CH_3COCH{=}CH_2 + SO_2 + 2HCl.$$

Halogenation of sodium 3-chlorobut-2-enesulphonate in an aqueous medium yields crystalline products [185,189,191], which Exner and Wichterle convincingly showed to be sulphones [189]:

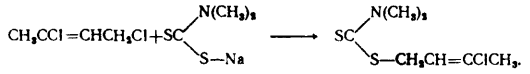
$$CH_3CCl{=}CHCH_2SO_3Na \xrightarrow[(H_2O)]{X_2} CH_3{-}\underset{\displaystyle O\ \ CH_2}{\overset{\displaystyle X\ \ X}{C{-}CH}}.$$
$$\qquad\qquad\qquad

with Na_2S. Allyl-(3-chlorobut-2-enyl) sulphide was synthesised similarly. Reaction of 1,3-dichlorobut-2-ene with Na_2S_2 yielded di-(3-chlorobut-2-enyl) disulphide, also as a mixture of two stereoisomers [200].

3-Chlorobut-2-enylmercaptoacetic acid was synthesised by the reaction of 1,3-dichlorobut-2-ene with mercaptoacetic acid in the presence of sodium hydroxide. It was then used to prepare 3-chlorobut-2-enylmercaptopenicillin, which proved to have antibiotic activity [201]. Other interesting sulphides derived from 1,3-dichlorobut-2-ene are products of the condensation of the latter with polysulphides, which have been proposed as softeners for varnishes and rubber [202].

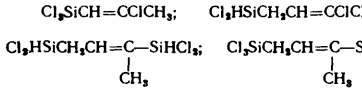
Among other sulphur-containing derivatives of 1,3-dichlorobut-2-ene, 3-chlorobut-2-enyl thiocyanate has been investigated in detail. This compound is readily obtained by the reaction of 1,3-dichlorobut-2-ene with a thiocyanate salt in an alcoholic [184] or aqueous alcoholic [203] medium. It has high insecticidal and acaricidal activity [203].

3-Chlorobut-2-enyl *NN*-dimethyldithiocarbamate, which may prove to be of interest as a fungicide, nematocide, and herbicide, was synthesised [204] by the reaction of 1,3-dichlorobut-2-ene with sodium *NN*-dimethyldithiocarbamate, as part of a series of syntheses of carbamates containing a 3-chlorobut-2-enyl group (analogues of the well-known insecticide Sevin):

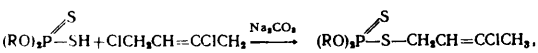


XI. SYNTHESIS OF ORGANOMETALLIC AND ORGANOMETALLOID COMPOUNDS

Among compounds of this type containing a 3-chlorobut-2-enyl group, those of silicon and phosphorus are known. Sadykh-Zade and Petrov showed that when 1,3-dichlorobut-2-ene is heated in a glass tube with an Si–Cu alloy, a complex mixture of chlorosilanes is formed [205], the following having been isolated in a pure state by fractional distillation:

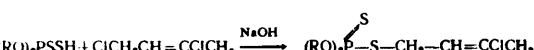


In his attempts to obtain insecticidal preparations, Tichý synthesised a series of *OO*-dialkyl *S*-(3-chlorobut-2-enyl) phosphorothiolothionates [206]:

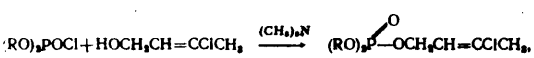


where R = CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9. According to his data, these compounds are less active than the well-known insecticide (acaricide) diethyl *p*-nitrophenyl phosphorothionate (Thiophos, Parathion).

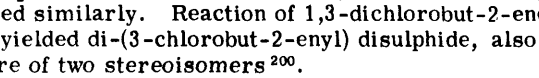
Apart from the phosphorothiolothionates, dialkyl 3-chlorobut-2-enyl phosphates, phosphorothionates, and phosphorothiolates have been synthesised at the Institute of Organoelemental Compounds of the USSR Academy of Sciences [207]:



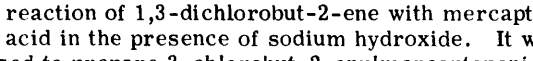
where R = CH_3 (74%), C_2H_5 (85%), or iso-C_3H_7 (67%);



where R = C_2H_5 (60%);



where R = C_2H_5 (60%) or iso-C_3H_7 (68%);



where R = C_2H_5 (35%). The compounds exhibit insecticidal activity on contact. The phosphorothionates and phosphorothiolates are the most active.

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The syntheses based on 1,3-dichlorobut-2-ene described above show that the latter can find a wide variety of applications both in industry and in preparative organic chemistry.

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THEORY OF CATALYTIC HYDROGEN WAVES IN ORGANIC POLAROGRAPHY

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I. INTRODUCTION

Catalytic hydrogen waves are an interesting phenomenon, frequently encountered in polarographic practice. They are associated with certain substances whose function is a catalytic one, since they assist the evolution of molecular hydrogen at the cathode without being altered by the electrode process. Catalytic hydrogen waves are observed at potentials less negative than the normal hydrogen waves for the given solution. The catalysts effectively lower the hydrogen overvoltage, thus accelerating (or catalysing) the evolution of hydrogen and justifying the use of the term "catalytic hydrogen waves".

Studies of catalytic waves can yield the rate constants for fast protolytic reactions, they can clarify adsorption phenomena at very low surface coverages, assess the rate of bimolecular free radical interactions, and quantitatively characterise the relationship between the structure of organic catalysts and their catalytic activity.

Catalytic hydrogen waves have also a practical interest. When applied to analytical problems, they enable conventional polarographic apparatus to be operated at the 10^{-7} M level, *i.e.* they raise the sensitivity of classical polarography by 2–3 orders of magnitude. The biological and medical applications of catalytic hydrogen waves are particularly interesting: they have made possible a number of diagnostic procedures such as Brdička's well-known serological polarographic test for cancer.

Herles and Vančura, in 1930, were the first to observe an unusual wave whilst studying the polarograms of blood serum solutions with sodium, potassium, and magnesium salts as supporting electrolytes. A report of these experiments was published, as a short communication[1], in 1932. Heyrovský and Babička repeated the work in 1930, and confirmed the appearance of new waves when proteins were