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THE CHEMISTRY OF SOME 1-SUBSTITUTED ALKA-1,3-DIENES

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I. INTRODUCTION

There are now many publications on the chemistry of the diene hydrocarbons. They are concerned mainly with the order of addition of various nucleophilic and electrophilic reagents, and also with developing ideas on the ability of dienes to form polymers, especially the industrially important buta-1,3-diene and isoprene rubbers.

The most recent views on the properties of dienes, and in particular of butadiene, are inseparably linked with their stereochemistry. Establishment of the *cis*- and *trans*--configurations of dienes is a most important contemporary stage in the evolution of diene chemistry. Conformational analysis makes it possible to obtain a deeper understanding of the various reactions of dienes, and also the structure and properties of the diverse derivatives of these compounds.

The present paper represents an attempt to give a systematic account of the most important investigations associated with various syntheses, leading ultimately to hetero--substituted buta-1,3-dienes.

II. 1-ALKOXYBUTA-1,3-DIENES

This section describes methods of synthesis and some chemical properties of compounds having the general formula

$$ROCH{=}CH{-}CH{=}CH_2.$$

These α-substituted butadienes can exist also as a pair of geometrical *cis*-*trans*-isomers.

1. Methods of Preparation

Existing methods for the synthesis of 1-alkoxybuta-1,3-dienes are based on various reactions of the following classes of organic compounds: acetals of unsaturated aldehydes, aldehydes and ketones, alkoxylated acetals of aldehydes, halogenated acetals of aldehydes, butenyne (vinylacetylene), and butadiyne (diacetylene).

Meier[1] was the first to obtain 1-methoxybuta-1,3-diene from the acetal of crotonaldehyde:

$$CH_3{-}CH{=}CH{-}CH(OCH_3)_2 \xrightarrow{-CH_3OH} CH_2{=}CH{-}CH{=}CHOCH_3.$$

The reaction was carried out in the presence of NaH_2PO_4 at 350°.

A new method was subsequently proposed[2] for synthesising 1-alkoxybuta-1,3-dienes by passing acetals of vinylacetaldehyde in the vapour phase over acid catalysts in a vacuum at 300°. The yield of the final product was ~45%:

$$CH_2{=}CH{-}CH_2{-}CH_2(OR)_2 \xrightarrow{-ROH} CH_2{=}CH{-}CH{=}CHOR.$$

Nazarov *et al.*[3] synthesised 1-ethoxy-3-methylbuta-1,3-diene by passing the vapour of 1,1-diethoxy-3-methylbut-2-ene (the diethylacetal of 3-methylcrotonaldehyde) over NaH_2PO_4 at 320°. The reaction is represented by the following scheme:

$$(H_3C)_2CH{-}CH_2{-}CHO \xrightarrow{Br_2;\,C_2H_5OH} (H_3C)_2CH{-}CHBr{-}CH(OC_2H_5)_2 \rightarrow$$

$$\xrightarrow{KOH} (H_3C)_2C{=}CH{-}CH(OC_2H_5)_2 \rightarrow CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CHOC_2H_5.$$

The same workers[3] obtained a 77% yield of an alkoxy-substituted isoprene by the catalytic cleavage of 1,1,3-triethoxy-3-methylbutane. The process of condensation and cleavage can be represented as follows:

$$(H_3C)_2C(OC_2H_5)_2 \xrightarrow{CH_2=CHOC_2H_5} (H_3C)_2\overset{OC_2H_5}{\overset{|}{C}}{-}CH_2{-}\overset{OC_2H_5}{\overset{|}{CH}}{-}OC_2H_5 \xrightarrow[\text{catalyst}]{t^\circ} CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CHOC_2H_5.$$

Condensation of the acetal with ethyl vinyl ether was effected at 0° in the presence of a catalytic quantity of the boron trifluoride–ether complex. The vapour of the resulting 1,1,3-triethoxy-3-methylbutane was passed over the contact catalyst $MgHPO_4$ at 350° and a pressure of 15–20 mm. A study of the efficiency of different catalysts for such cleavage reactions showed the best results to be obtained on $MgHPO_4.Na_2SiO_3$ catalysts deposited on activated charcoal. Several other 1-alkoxybuta-1,3-dienes have been obtained in a similar manner[1,4,5].

Alkoxy-dienes can be prepared also by other methods. Wichterle[6] observed that the acetal of chlorobutyraldehyde decomposes under the action of metallic potassium to yield 1-alkoxybuta-1,3-dienes

$$CH_3CHClCH_2CH(OR)_2 \xrightarrow[-HCl]{-ROH} CH_2{=}CH{-}CH{=}CHOR + CH_3CH{=}CH{-}CH(OR)_2.$$

Potassium alkoxides add on smoothly to the triple bond in butenyne[7] forming mainly 1- and 2-alkoxybuta-1,3-dienes and also a small amount of the 1,1-dialkoxybut-2-ene.

$$CH_2{=}CH{-}C{\equiv}CH + ROH \longrightarrow \begin{cases} CH_2{=}CH{-}\overset{OR}{\overset{|}{C}}{=}CH_2\ (10\%) \\ CH_2{=}CH{-}CH{=}CHOR\ \text{(main product)} \\ CH_3{\cdot}CH{=}CH{-}CH(OR)_2\ \text{(small amount)}. \end{cases}$$

Shostakovskii *et al.*[8,9] worked out a new method for the synthesis of alkoxybuta-1,3-dienes, consisting in the selective hydrogenation of alkyl but-1-en-3-ynyl ethers, which can be represented as follows:

$$HC{\equiv}C{-}C{\equiv}CH + ROH \rightarrow HC{\equiv}C{-}CH{=}CHOR \xrightarrow{H_2} CH_2{=}CH{-}CH{=}CHOR.$$

Hydrogenation of butenynyl ethers takes place in methanolic solution over palladium (on gypsum) at room temperature.

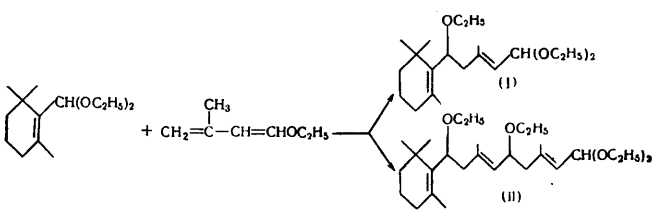
2. Some Chemical Reactions of 1-Alkoxybuta-1,3-dienes

(a) Condensation. Alkoxy-dienes, like other vinyl ethers, undergo condensation reactions. Nazarov and Krasnaya[10] were the first to effect the condensation of acetals with ethoxyisoprene and with ethoxybutadiene:

$$CH_3{-}\overset{R}{\overset{|}{C}}{=}CH + CH_2{=}CH{-}CH{=}CHOC_2H_5 \longrightarrow$$

$$\rightarrow \begin{cases} (H_3C)(R)C{=}CH{-}\overset{OC_2H_5}{\overset{|}{C}}H{-}CH_2CH{=}CH{-}CH(OC_2H_5)_2 \\ (H_3C)(R)C{=}CH(CHCH_2CH{=}CH)_2{-}CH(OC_2H_5)_2 \\ (H_3C)(R)C{=}CH(-CHCH{=}CH)_3{-}CH(OC_2H_5)_2. \end{cases}$$

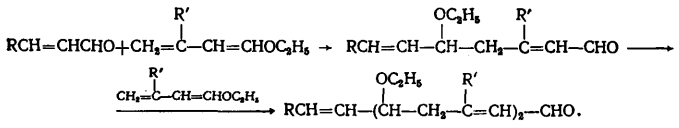
These reactions take place under the influence of boron trifluoride–ether at 0°–5°. Ethoxyisoprene undergoes condensation far more readily than does ethoxybutadiene, and gives a high yield of the final products. These workers were able to lengthen the carbon chain by 5–10 carbon atoms, and correspondingly increase the number of conjugated double bonds.



Considerable interest attaches to the condensation with ethoxyisoprene of the acetal of β-cyclo-citral[11], which opens up a path for the synthesis of several biologically active substances. This reaction takes place at 40°–55°. The corresponding reactions with (I) yield ethoxydihydro-β-ionylideneacetaldehyde and the corresponding alcohol,

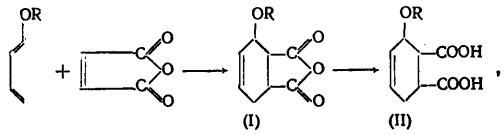
while from the substance (II) high yields of the diethoxybisdehydroaldehyde of Vitamin A and diethoxybisdehydrovitamin A have been synthesised.

Krasnaya and Kucherov [12] condensed various aldehydes with alkoxy-dienes



Formation of unsaturated alkoxy-aldehydes in this way goes well in the presence of boron trifluoride, zinc chloride, and boric acid.

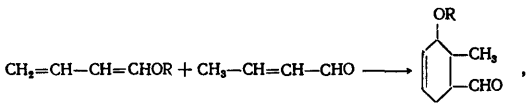
(b) Diene synthesis. 1-Alkoxybuta-1,3-dienes readily take part in diene synthesis with maleic anhydride [13-15]:



where R = C_2H_5. A similar condensation has been carried out with 1-methoxybuta-1,3-diene and 1,4-diethoxybuta-1,3-diene, giving the corresponding cyclic anhydrides, and also with 1-butyl- and 1-isopentyl-buta-1,3-diene [2].

Farmilo and Nicholls [4] undertook the condensation of a mixture of *cis*- and *trans*-1-methoxybuta-1,3-diene with maleic anhydride, and found that only the *trans*-isomer forms an adduct. In their view this reaction can be utilised for the separation of geometrical isomers.

Shostakovskii *et al.* [9] condensed 1-cyclohexyloxybuta-1,3-diene with maleic anhydride, and found that formation of the adduct was accompanied by copolymerisation of the anhydride with butadiene. As a result, a copolymer was isolated which probably had a regular structure. Condensation of 1-alkoxybuta-1,3-dienes with crotonaldehyde [9], however, gave aldehydes of methylalkoxycyclohexenes:



where R = C_4H_9, C_6H_{11}.

The above work shows that geometrical isomerism has a considerable influence in the diene condensation of 1-alkoxybuta-1,3-dienes, only the *trans*-isomers undergoing condensation. Diene condensations are accompanied by heteropolymerisation. The reason for this must obviously be sought in the behaviour of the *cis*-isomer of the original alkoxybuta-1,3-diene.

The polymerisation of 1-alkoxybuta-1,3-dienes has not been investigated systematically, and the literature contains only isolated and contradictory observations. Thus Wichterle [16] was the first to note that 1-ethoxybutadiene undergoes polymerisation on standing. Other workers [5] observed considerable polymerisation of 1-methoxybuta-1,3-diene even on distillation. Flaig [15] showed that 1-alkoxybutadienes are difficult to polymerise. This is fully consistent with the general rule that butadiene is more strongly activated by substituents in position 2 than in position 1. Thus in the absence of air, for example, pure 1-alkoxybutadienes take months to polymerise. In air or in the presence of peroxides, polymerisation takes place with the formation of products of high molecular weight.

III. SULPHUR-CONTAINING BUTA-1,3-DIENES

1. Methods of Synthesis

Existing methods for the synthesis of sulphur-containing buta-1,3-dienes are based on various reactions of butadiene and butadiyne, thiols, and also alcohols and phenols.

A study of the effect of various reaction conditions showed [17,18] that addition of the thiol takes place merely on gentle heating of a mixture containing butadiyne in the presence of potassium hydroxide:

$$HC{\equiv}C{-}C{\equiv}CH + RSH \longrightarrow HC{\equiv}C{-}CH{=}CHSR.$$

The resulting alkenyne can add on a further thiol molecule, giving 60-90% yields of 1,4-dialkylthiobuta-1,3-dienes:

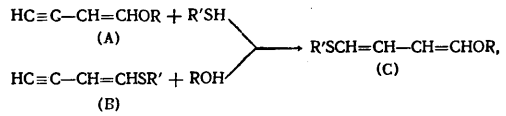
$$HC{\equiv}C{-}CH{=}CHSR + RSH \longrightarrow RSCH{=}CH{-}CH{=}CHSR.$$

Addition of the second thiol molecule takes place more readily on heating and under the influence of radical initiators.

Prilezhaeva *et al.* [19] made a detailed study of this reaction. They discovered also that, if two thiols are taken, formation of the mixed buta-1,3-diene sulphides is accompanied by a symmetrisation of the unsymmetrical dienes:

$$RSCH{=}CH{-}C{\equiv}CH + R'SH \longrightarrow RSCH{=}CH{-}CH{=}CHSR',$$
$$2RSCH{=}CH{-}CH{=}CHSR' \longrightarrow R'SCH{=}CH{-}CH{=}CHSR' + RSCH{=}CH{-}CH{=}CHSR,$$

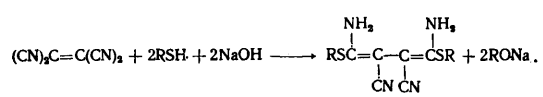
where R = CH_3, C_2H_5, C_4H_9; R' = C_4H_9. The yield of individual dialkylthiobutadienes reached 77%. Sulphur-containing dienes have been prepared also by the reaction of alkyl but-1-en-3-ynyl ethers with thiols and of alkyl but-1-en-3-ynyl sulphides with alcohols [20]:



where R = C_4H_9, C_6H_{11}, $C_6H_5CH_2$; R' = C_2H_5, C_6H_5.

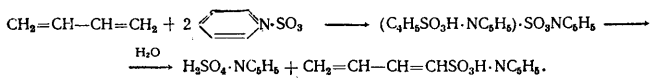
Thiols were found to add on smoothly to alkyl but-1-en-3-ynyl ethers (scheme A), converting the latter into alkyl (or aryl) thiobutadienyl ethers (product C). In the case of ethanethiol, addition to alkyl but-1-en-3-ynyl ethers is carried out in the presence of azodiisobutyronitrile at 75°-80°, and good yields of the corresponding alkylthiobutadienyl ethers are obtained. In several cases the yield was lower in the presence of KOH. This indicates that the reaction takes place by a radical mechanism. However, attempts to effect addition of the alcohol to the but-1-en-3-ynyl sulphide (scheme B) under the above conditions were unsuccessful.

Alkylthiobutadienes have been obtained also by the condensation of thiols with tetracyanoethylene [21]. Yields of up to 80% of 1,4-dialkylthio-1,4-diamino-2,3-dicyanobuta-1,3-dienes were synthesised in this case. The reaction can be represented by the general equation:

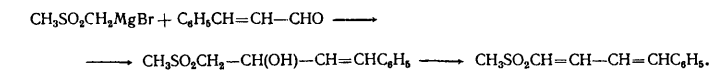


The work of Terent'ev and Dombrovskii[22-31] has shown that the pyridine–sulphur trioxide complex is an excellent sulphonating agent for monoalkenes and dienes containing an activated double bond. Sulphonation takes place when a mixture of the components in dichloroethane solution is heated at 100° – 120° for several hours.

These workers found[29] that, in the sulphonation of compounds containing conjugated double bonds, two molecules of this sulphonating agent first add on to one molecule of the initial compound, with subsequent elimination of a pyridinium sulphate molecule by hydrolysis. The mechanism of this reaction can be written, in the case of butadiene:

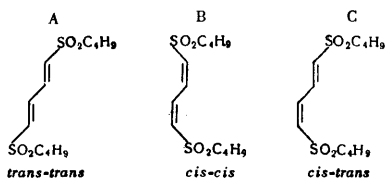


Dienes containing a sulphone grouping have been obtained[32] by organomagnesium synthesis, as follows:



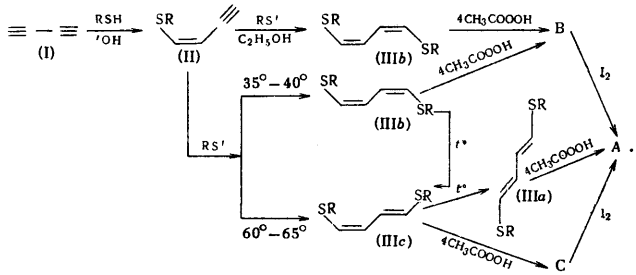
2. Some Chemical Reactions of Sulphur-Containing Buta-1,3-dienes

Prilezhaeva *et al.*[33] converted dibutylthiobuta-1,3-diene into a crystalline sulphone by oxidising it with acetyl hydroperoxide in ethereal solution at low temperatures. From the mixture of sulphones were isolated three possible geometrical isomers of dibutylsulphonylbuta-1,3-diene:



These workers effected in high yield the stereospecific ionic addition of a thiol to 1-butylthiobut-1-en-3-yne (II) with formation of the practically pure *cis* - *cis* isomer (III*b*). This takes place only with as complete removal as possible of air from the reaction medium, the use of inhibitors, and also, if the whole of the thiol is converted into a metal salt, on prolonged heating in ethanol.

When the reaction was carried out under conditions favouring a free-radical addition (with the free thiol, in the presence of air, and with an inert solvent as diluent), mixtures of III*b* and III*c* were obtained in which the latter predominated. On being heated in the presence of oxygen, III*b* partly isomerises into III*c*. Thus the free-radical addition of butanethiol to II is non-stereospecific. If conditions are such that there is competition between free-radical and ionic mechanisms (simultaneous presence of free thiol, a metal salt of the thiol, and air), reaction takes place slowly and mainly by the free-radical mechanism. Under these conditions III*a* appears in the reaction mixture, probably resulting from the isomerisation of III*c*. The stereochemical relations in this reaction are represented by the following scheme:



Oxidation of dialkyl(or aryl)thiobuta-1,3-dienes[34] yields the corresponding disulphones of general formula RSO_2CH : :CHCH : $CHSO_2R$. These disulphones have been isolated in good yield, and are stable crystalline substances, the structures of which have been demonstrated spectroscopically.

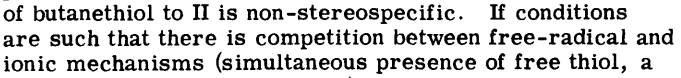
Stereochemical orientation in the synthesis of 1,4-dialkylthiobuta-1,3-dienes has been studied[35] with butadiyne and benzenethiol as components. The reaction was carried out under different conditions ensuring an ionic, a radical, or a mixed type of mechanism. Geometrical stereoisomers were isolated as crystalline substances, which were subjected to subsequent oxidation, isomerisation, and optical examination. In the case of 1,4-diethylthiobuta-1,3-diene with cyclopentadiene[36], diene synthesis takes place in stages and is accompanied by the formation of adducts containing different numbers of cyclopentadiene molecules per molecule of the diethylthiobutadiene. The proportions of the adducts obtained depend on those of the starting materials and on the duration of heating. In contrast to the analogous condensation with maleic anhydride, the adducts which are now formed do not split off ethylthio-groups. Elimination would obviously have led to aromatisation of the ring[17,20] and would have indicated that the cyclopentadiene, not the original diene, was acting as the dienophil.

IV. NITROGEN-CONTAINING BUTA-1,3-DIENES (METHODS OF SYNTHESIS)

The reactivity of buta-1,3-dienes containing nitrogen varies greatly with their composition and structure, and such compounds therefore exhibit great diversity. From our present point of view it is useful to discuss them in the order: amino-derivatives, nitro-derivatives, and cyano-derivatives of buta-1,3-diene.

1. Amino-Substituted Buta-1,3-dienes

Relatively little work has been done on the synthesis of monoamino-1,3-dienes. 1-Amino-4-phenylbutadiene was first synthesised by the action of sodamide (potassium) on 1-bromo-4-phenylbutadiene in liquid ammonia[37]:



Langenbeck *et al.*[38] found that piperidine reacts with crotonaldehyde to form 1,3-dipiperidinobut-2-ene, which

on being heated splits into piperidine and 1-piperidinobuta-1,3-diene:

$$CH_3CH{=}CH{-}CHO + 2HNC_5H_{10} \longrightarrow CH_3CH(NC_5H_{10})CH{=}CH(NC_5H_{10}) \xrightarrow{130^\circ}$$
$$\longrightarrow CH_2{=}CH{-}CH{=}CHNC_5H_{10} + HNC_5H_{10}.$$

The reaction is carried out in absolute ether in the presence of anhydrous potassium carbonate. Other monoaminated 1,3-dienes have been obtained by analogous methods in yields of 15–40%.

It is stated in a patent[39] that dialkylaminobuta-1,3-dienes are obtained by passing 1,4-bisdialkylaminobut-2-ynes in the vapour phase over various catalysts and finely dispersed metallic sodium. The reaction can be represented by the general equation:

$$R'_2NCH_2{-}C{\equiv}C{-}CH_2NR'_2 \xrightarrow[\text{catalyst, } t^\circ]{} R'_2NCH{=}CH{-}CH{=}CHNR'_2,$$

where R = CH_3 and R′ = C_2H_5.

This reaction goes at 250°–450° in the presence of chromium and aluminium oxides and other catalysts, giving yields up to 80%, and is accompanied by isomerisation, the mechanism of which has not yet been adequately studied. It may perhaps represent an acetylene–diene rearrangement, as has been shown in the case of 1,4-dichlorobut-2-yne[40].

1,4-Bisdialkylaminobuta-1,3-dienes having a more branched structure:

$$R_2N{-}\underset{\displaystyle R'}{\underset{|}{C}}{=}CH{-}CH{=}\underset{\displaystyle R''}{\underset{|}{C}}{-}NR_2$$

have also been obtained[41,42].

A new method has recently been worked out for the synthesis of 1,4-bisalkylaminobuta-1,3-dienes from butadiyne and various amines[43–45]:

$$2RNH_2 + HC{\equiv}C{-}C{\equiv}CH \longrightarrow RNHCH{=}CH{-}CH{=}CHNHR.$$

This method gives a high yield (80%) of the final product, and is simple to carry out experimentally, since reaction occurs very smoothly at room temperature.

With secondary amines stepwise addition takes place, 1-dialkylaminobut-1-en-3-ynes being first formed according to the equation:

$$R_2NH + HC{\equiv}C{-}C{\equiv}CH \longrightarrow R_2NCH{=}CH{-}C{\equiv}CH.$$

Addition of a second molecule of the amine to this product requires more severe conditions[45]. Thus n-pentylamine adds on to but-1-en-3-ynyldiethylamine at the boiling point of the alkenyne. The temperature can be lowered by carrying out the reaction under vacuum:

$$(C_2H_5)_2NCH{=}CH{-}C{\equiv}CH + H_2NC_5H_{11} \longrightarrow (C_2H_5)_2NCH{=}CH{-}CH{=}CHNHC_5H_{11}.$$

The main products and the direction of the reaction are governed by the nature of the initial amines.

2. Nitro-Substituted Buta-1,3-dienes

The literature contains only one reference[46] to the preparation of 1-nitrobuta-1,3-diene, which was obtained by the direct action of nitric acid on the diene:

$$CH_2{=}CH{-}CH{=}CH_2 + HONO_2 \longrightarrow CH_2{=}CH{-}CH{=}CHNO_2.$$

1,4-Dinitro-derivatives of 1,3-dienes have been obtained by other methods.

Perekalin and Lerner[47] obtained a 40% yield of 1,4-dinitrobuta-1,3-diene from dinitro-derivatives of ethylenic hydrocarbons:

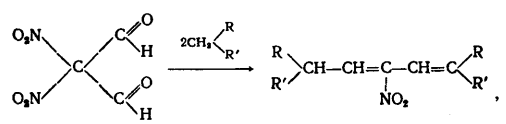
$$CH_2{-}CH{=}CH{-}CH_2 \xrightarrow{Cl_2} CH_2{-}CHCl{-}CHCl{-}CH_2 \xrightarrow{(CH_3COO)_4Pb} CH{=}CH{-}CH{=}CH.$$
$$\quad NO_2 \qquad\quad NO_2 \qquad\quad NO_2 \qquad\quad NO_2 \qquad\quad NO_2 \qquad\quad NO_2$$

Novikov *et al.*[48] prepared the same product by condensing glyoxal with nitromethane, the yield being quantitative:

$$OCH{-}CHO \xrightarrow{CH_3NO_2} CH_2{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}CH_2 \xrightarrow{CH_3COCl}$$
$$\longrightarrow CH_2{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}\underset{\displaystyle NO_2}{\underset{|}{CH}}{-}CH_2 \xrightarrow{KHCO_3} CH{=}CH{-}CH{=}CH.$$
$$\quad OCOCH_3 \quad OCOCH_3 \qquad\qquad NO_2 \qquad\quad NO_2$$

Attempts at the direct synthesis of 1,2,3,4-tetranitrobuta-1,3-diene from butadiyne and dinitrogen tetroxide[49] have so far been unsuccessful, since the reaction has been accompanied by explosions. The only product which could then be isolated was oxalic acid.

Perekalin[50] has also worked out a method for synthesising several nitrobuta-1,3-diene derivatives based on the condensation of the sodium salt of nitromalonaldehyde with various substances containing reactive hydrogen atoms in methylene or methyl groups:



where R = C_2H_5COO, CN and R′ = CN, NO_2. In this way mono- and di-nitro-derivatives of 1,3-dienes have been obtained containing aromatic and heterocyclic radicals in the carbon chain.

Kochetkov and Dudykina[51] synthesised 1-nitro-4-phenylbuta-1,3-diene in yields up to 66% by the reaction of cinnamaldehyde with nitromethane

$$C_6H_5CH{=}CH{-}CHO + CH_3NO_2 \xrightarrow{-H_2O} C_6H_5CH{=}CH{-}CH{=}CHNO_2.$$

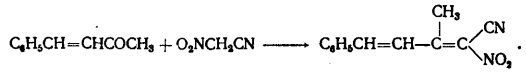
The action of N_2O_4 on phenylated dienes under various conditions gave good yields of the following dinitrobuta-1,3-dienes[52–54]:

(*a*) $C_6H_5CH{=}CH{-}CH{=}CHC_6H_5 \xrightarrow{N_2O_4} C_6H_5CH{-}CH{=}CH{-}CHC_6H_5 \longrightarrow$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad NO_2 \qquad\qquad NO_2$

$$\xrightarrow[NH_4OH]{dil.} C_6H_5C{=}CH{-}CH{=}CHC_6H_5,$$
$$\qquad\qquad\qquad\qquad\quad NO_2$$

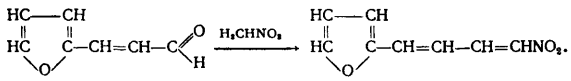
(*b*) $C_6H_5C{=}CH{-}CH{=}CC_6H_5 \xrightarrow[\text{abs. ether, cooled}]{N_2O_4} C_6H_5C{=}CH{-}CH{=}C\,C_6H_5$
$\qquad\quad NO_2 \qquad\quad H \qquad\qquad\qquad\qquad\quad NO_2 \qquad\qquad NO_2$

Condensation of methyl phenylvinyl ketone with nitroacetonitrile gives a 65% yield of 2-methyl-1-nitro-4--phenylbuta-1,3-dienyl cyanide[55]:



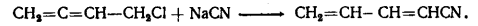
Methylamine and diethylamine act as catalysts for this reaction.

Condensation of furylacraldehyde with nitromethane provides a synthesis of 1-(2-furyl)-4-nitrobuta-1,3-diene[56]



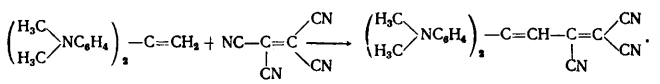
3. Cyano-Substituted Buta-1,3-dienes

Numerous papers have been published on methods of synthesising and the chemical properties of dienes containing one, two, or more cyano-groups. These methods and properties can differ greatly depending on the number of cyano-groups and their positions in the molecule, and also on the stereoisomerism of the diene system itself. Patent claims and several investigations[57-62] have been made on the synthesis of 1-cyanobuta-1,3-diene. According to Coffman[62], for example, this compound is obtained as follows:

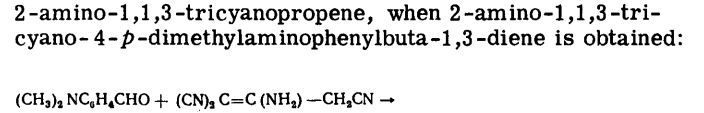


The reaction is carried out in methanol with gentle heating. In the light and also on standing, the reaction product polymerises, the resulting polymer resembling ω-polychloroprene.

Cyanobutadienes can be synthesised by the interaction of 1,1-bis-*p*-dimethylaminophenylethylene and tetracyanoethylene[63], which yield 3,4,4-tricyano-1,1-bis-*p*-dimethylaminophenylbuta-1,3-dienes. The principal reaction can be represented by the equation:



The same workers obtained a series of compounds of this type, differing in the numbers of dimethylaminophenyl and cyano-groups in the butadiene structure. There are also indications in patents[64,65] that such dienes can be obtained by the interaction of *p*-dimethylaminobenzaldehyde and 2-amino-1,1,3-tricyanopropene, when 2-amino-1,1,3-tricyano-4-*p*-dimethylaminophenylbuta-1,3-diene is obtained:

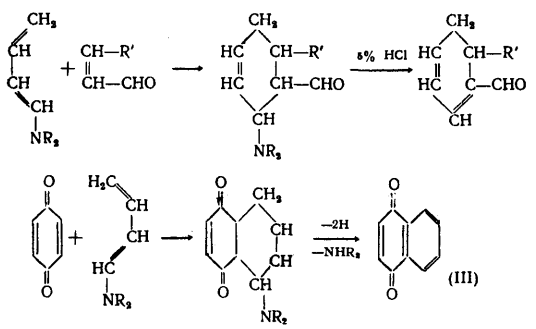


4. Some Chemical Reactions of Nitrogen-Containing Buta--1,3-dienes

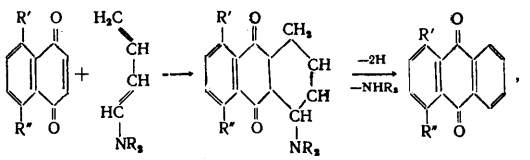
Among the typical reactions of compounds containing a system of conjugated double bonds is their ability to condense with various unsaturated compounds in which the multiple bond is activated by so-called electronegative groups such as C=O, C≡N, NO_2, etc.

In order to determine the effect of a nitro-group on the conjugated system of a diene, 1-nitrobuta-1,3-diene was prepared by the direct nitration of butadiene[66], and its reactivity with maleic anhydride was studied. It was concluded that the diene system in the nitrodiene had been deactivated, especially the αβ-double bond, as a result of which nitrobutadiene acts as a nitroalkene in additions.

Many investiations have been made on diene syntheses involving aminobuta-1,3-dienes and various dienophils[38,67]. Thus Langenbeck *et al.*[38] found that diene synthesis goes well with 1-aminobutadienes and compounds which are not acidic in character but contain a reactive double bond. Dienophils which are acidic in character result in rapid resinification of the aminobutadienes. Acraldehyde yields dihydrobenzaldehyde (I), crotonaldehyde gives dihydro-*o*-tolualdehyde (II), benzoquinone produces naphthaquinone (III), and from α-naphthaquinone is obtained anthraquinone (IV) and correspondingly naphthazarin passes into quinizarin (V).

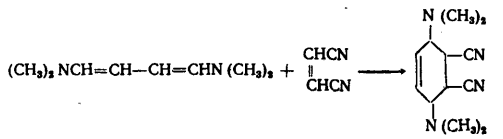


for (I), R′ = H; and (II) R′ = CH_3.

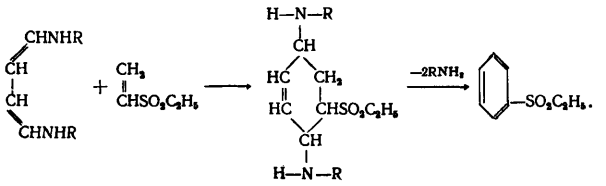


for (IV), R′ = R″ = H; and (V), R′ = R″ = OH.

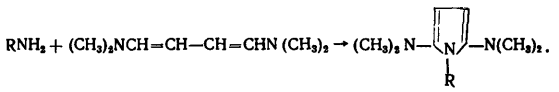
Some work has been done also on the chemistry of 1,4--diaminobuta-1,3-dienes. Thus Fegley *et al.*[68] studied the reaction of *cis-trans*- and *trans-trans*-isomers with dienophils containing electron-acceptor groups adjacent to the double bond. 1,4-Bisdimethylaminobuta-*cis*-1, *trans*-3--diene with fumaronitrile gives *cis-trans* (or *trans-cis*)--3,6-bisdimethylaminocyclohex-4-ene-*cis-trans*-1,2-dicarbonitrile. 1,4-Bisdimethylaminobuta-*trans*-1,*trans*-3--diene gives with the same dienophil *cis-cis*-3,6-bisdimethylaminocyclohex-4-ene-*cis-trans*-1,2-dicarbonitrile.



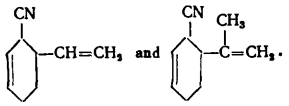
1,4-Diaminobutadienes undergo diene condensation also with ethyl vinyl sulphone[45]:



Among other chemical properties, the reactions of 1,4--diaminodienes with various amines have been studied. With primary amines *N*-substituted pyrroles are formed[69]:

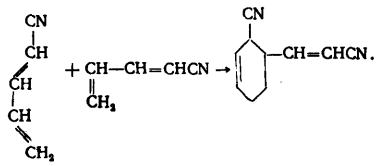


With 1-cyanodienes the general rule remains valid that the *cis*-isomer does not undergo condensation at all with maleic anhydride, whereas its *trans*-isomer gives an adduct in good yield[70]. With cyclopentadiene[71] as dienophil, both *cis*- and *trans*-isomers of the original cyanodiene give the corresponding adducts, in yields of 58 and 80% respectively under identical conditions. Butadiene and isoprene as dienophils[72] yield adducts having the structures:



A study of the dimerisation of monocyanodienes has shown[73] that *trans*-1-cyanobuta-1,3-diene is the main source of the dimer, whereas the *cis*-isomer is converted comparatively readily into a polymeric product.

Dimerisation of this diene can be represented in general as:



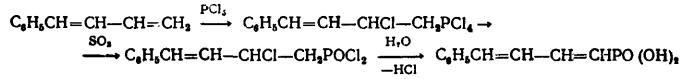
V. HETERO-SUBSTITUTED PHOSPHORUS-CONTAINING BUTA-1,3-DIENES

Under this name we are concerned with organic compounds having a butadiene carbon chain and containing other elements as well as phosphorus. Such compounds have been synthesised only during the past few years.

1. Methods of Preparation

One of the first papers on the synthesis of organophosphorus 1,3-dienes was that by Bergmann and Bondi[74], who obtained 4-phenylbuta-1,3-dienylphosphonic acid from 1-phenylbuta-1,3-diene and phosphorus pentachloride.

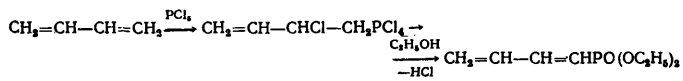
After appropriate treatment of the intermediate complex with dry sulphur dioxide followed by water, the organophosphorus diene was isolated:



However, the mechanism of the reaction and also the structure of the product have not been rigorously proved.

Papers by Kosolapoff and others[75,76] suggest that, when phosphorus pentachloride reacts with compounds containing double bonds, a chlorine atom adds on to the least hydrogenated carbon atom, while the PCl_4 group becomes attached to the most hydrogenated carbon atom.

Phosphorus pentachloride adds on in this way to butadiene, and the preparation of ethyl butadienylphosphonate in this way has been patented[77].



Dehydrochlorination of the intermediate product is effected with alcoholic potassium hydroxide.

Anisimov and others considerably extended the addition of phosphorus pentachloride to various unsaturated compounds, in particular to diene hydrocarbons[78,79].

Organophosphorus acid chlorides were converted into esters by reaction with alcohols in the presence of pyridine[80].

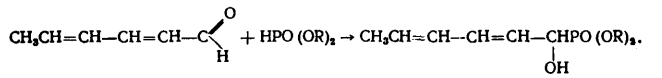
Organophosphorus dienes have been obtained also from alkynes. Zinov'ev *et al.*[81] studied the reaction of acetylenic hydrocarbons with phosphorus trichloride and oxygen, and found that a halogen atom and the $POCl_2$ group add on to the acetylenic bond with the formation of dienes.

Petrov *et al.*[82] added phosphorus pentachloride to hex--1-en-5-yne.

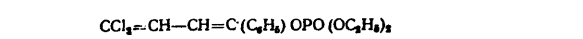
Vovsi *et al.*[83] first carried out the reaction of phosphorus pentachloride with 2-methylbut-1-en-3-yne.

Anisimov and his coworkers effected the addition of phosphorus pentachloride to ethynylcyclohexene[84] and to 2-methylbut-1-en-3-yne[85]. They also studied the properties of the resulting diene acid chlorides, which, as was to be expected, reacted readily with alcohols to yield the normal esters. Organophosphorus dienes have been obtained also by the addition of phosphoric esters to polyenes.

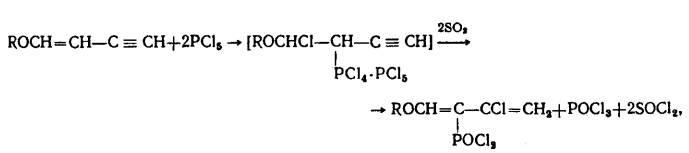
Pudovik and Kitaev[86] synthesised multifunctional phosphorus-containing 1,3-dienes by the reaction:



Allen and Johnson[87] prepared a diene containing phosphorus and an aromatic radical, and having the following structure:

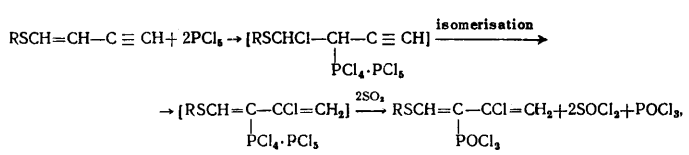


Hetero-substituted organophosphorus dienes have been obtained also from alkyl but-1-en-3-ynyl ethers[88]:



where R = CH_3, C_2H_5, C_3H_7, C_4H_9. The structures of the resulting compounds were proved from their Raman spectra[89]. Esters and amides of these acid chlorides have also been prepared[90].

A continuation of an investigation[88] which had been begun on this class of organic compounds was the synthesis[91] of 1-alkylthio-3-chloro-2-dichlorophosphinylbuta-1,3-dienes by the scheme:



where R = CH_3, C_2H_5, C_3H_7, C_4H_9.

The structure of these derivatives was established from their infra-red spectra. Several of their chemical properties were also studied, and in particular their normal esters, amides, thiols, and other derivatives were synthesised[92-94].

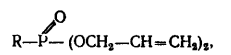
2. Some Chemical Properties

Among the chemical properties of organophosphorus monomers, special significance attaches to their conversion into compounds of high molecular weight, many of which are widely used in various branches of the national economy. During recent years the chemistry of macromolecular organophosphorus compounds has been developed more intensively. Much research has been done on the polymerisation and copolymerisation of esters and amides of various phosphoric acids. It has been discovered that compounds of high molecular weight can be obtained comparatively easily from allyl and methylallyl esters of phosphonic acids.

In 1940 Warren[95] and Toy[96-97] discovered that allyl and methylallyl arylphosphonates could be polymerised to transparent, flameproof, vitreous materials. The formation of polymers was substantially affected by the structure and number of individual groups in the original monomer. Thus esters of phosphorus acids containing one allyl group form only products of low molecular weight at the best. Compounds containing two allyl groups are readily polymerised from the initial monomer[98-102].

It can be assumed from the work of several investigators[101,103-105] that the tendency to polymerisation of allyl and methylallyl esters of phosphorus acids, and the properties of the resulting polymers, will be influenced by the following factors: (a) the molecular weight of the monomer and the size of the substituents attached to the phosphorus atom, (b) the electronic character of these substituents, and (c) the presence or absence of inhibiting groups in the ester molecule.

Thus among compounds of the general formula



where the substituents (R) may be H, CH_3, C_2H_5, C_3H_7, iso-C_3H_7, or C_4H_9, those in which R is smallest in size will form a solid polymer, and as R becomes more bulky the hardness of the polymers will diminish until they become gelatinous. The hardness of the resulting polymer diminishes as the ester part of the monomer molecule becomes larger. Under such conditions the increase in molecular weight of the monomer probably has an effect, under otherwise identical conditions, of impeding polymerisation.

The hardness of the above polymers is substantially affected by the electronegativity of the substituent. Thus vitreous polymers are obtained from those allyl esters in which the electronegativity of the substituent directly combined with the phosphorus is greater than that of the methyl group (isobutenyl, aryl, benzyl, phenoxy, etc. group).

The presence of some atoms or groups in the allyl esters of phosphorus acid inhibits polymerisation, allowing at best viscous syrups or oils to be obtained, but not solid polymers. Among such inhibiting atoms or groups are sulphur and nitrogen located between the phosphorus and the allyl groups[106].

There are indications[99,101] that the presence of several double bonds in allyl arylphosphonates does not always make these substances capable of polymerisation. In spite of this, however, other investigators have obtained transparent solid polymers from diallyl arylphosphonates[100,106-108].

The ability of vinyl esters of phosphorus acids to form polymers has been investigated by Upson[109], Gefter and Kabachnik[110], and others[111,112]. Compounds of this type containing two or three double bonds yielded hard vitreous polymers on being heated in the presence of benzoyl peroxide. Esters containing only one double bond, however, either do not polymerise at all or else give viscous liquids or gelatinous masses.

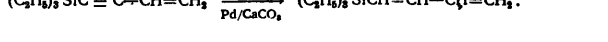
VI. SILICON-CONTAINING BUTA-1,3-DIENES

In view of the vigorous development of the silicon industry, it is of particular importance to work out new methods for the synthesis and investigation of the chemical properties of organosilicon monomers, and among such monomers the silicon-substituted buta-1,3-dienes occupy a special position. It therefore seemed to us interesting to summarise the literature on this question.

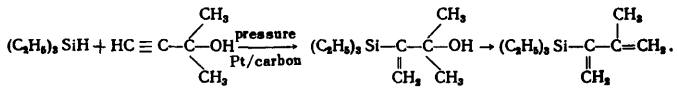
1. Methods of Preparation

Existing paths for the synthesis of silicon-substituted buta-1,3-dienes are based on various chemical reactions of the following organic starting materials: chloroprene and vinylacetylene (but-1-en-3-yne), trialkylsilanes, acetylenic alcohols containing silicon, and finally simple silanes.

Petrov and Sadykh-zade[113] synthesised triethylsilyl-1-butadiene by the selective hydrogenation of 4-triethylsilylbut-1-en-3-yne over palladium on $CaCO_3$:

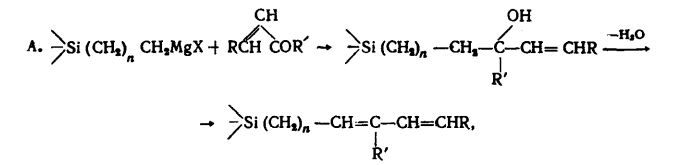


Shchukovskaya *et al.*[114] obtained a diene containing silicon by the dehydration of an unsaturated alcohol containing silicon:

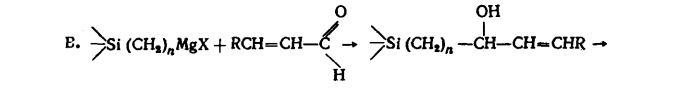


The organosilicon alcohol used as starting material was synthesised at elevated pressures and with platinum on activated charcoal as catalyst.

Sadykh-zade and Petrov[115,116] obtained various trialkylsilylbuta-1,3-dienes by a similar method:



where n = 2,6; R = H, CH_3, C_6H_5; R′ = H, CH_3.



where n = 1,3; R = H, CH_3, C_6H_5.

The alcohols were dehydrated by the action of $KHSO_4$.

It was subsequently shown[117] that silylbutadienes can be synthesised by the addition of silanes to but-1-en-3-yne at room temperature:

$$CH_3Cl_2SiH + HC\equiv C-CH=CH_2 \rightarrow CH_3Cl_2SiCH=CH-CH=CH_2,$$
$$Cl_3SiH + HC\equiv C-CH=CH_2 \rightarrow Cl_3SiCH=CH-CH=CH_2.$$

The best catalyst for such reactions proved to be a 0.01 N solution of chloroplatinic acid in isopropyl alcohol, *i.e.* the so-called Speier catalyst[118].

Several organosilicon dienes were obtained by Shostakovskii *et al.*[119]. These workers synthesised 1-butoxy-4-trimethylsilylbuta-1,3-diene by the selective hydrogenation of 1-butoxy-4-trimethylsilylbut-1-en-3-yne:

$$(CH_3)_3SiC\equiv C-CH=CHOR \xrightarrow{H_2} (CH_3)_3SiCH=CH-CH=CHOR.$$

The hydrogenation was catalysed with a mixture of 2% Pd on $CaCO_3$ and 5% Pt on carbon.

2. Some Chemical Reactions of Silicon-Containing Buta-1,3-dienes

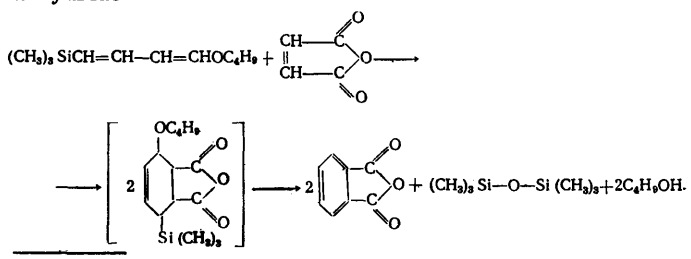
The literature on the synthesis and the properties of organosilicon dienes is very limited. This interesting branch of diene chemistry is in the initial stages of its development.

Alkylation of appropriate organosilicon butadienes can be achieved by replacing reactive chlorine atoms, for example, by methyl groups[120]:

$$CH_3Cl_2SiCH=CH-CH=CH_2+2CH_3MgI \rightarrow (CH_3)_2SiCH=CH-CH=CH_2+2MgICl,$$
$$Cl_3SiCH=CH-CH=CH_2+3CH_3MgI \rightarrow (CH_3)_3SiCH=CH-CH=CH_2+3MgICl.$$

A study was made of the tendency of the above silicon-containing diene hydrocarbons to undergo condensation and dimerisation[121]. Silylbutadienes were condensed with acraldehyde, methyl acrylate, and acrylonitrile. In all cases good yields of the corresponding cyclic adducts were obtained.

Shostakovskii *et al.*[119] have condensed 1-butoxy-4-trimethylsilylbuta-1,3-diene with maleic anhydride. The resulting cyclic adduct is unstable, and butanol is already eliminated under the reaction conditions. In the end it was possible to isolate only hexamethyldisiloxane and phthalic anhydride:



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FREE RADICAL REACTIONS IN THE ELECTROLYSIS OF ORGANIC COMPOUNDS

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1. INTRODUCTION

Electrolytic processes in aqueous and non-aqueous electrolytes often lead to the formation of free radicals. Free radical reactions during electrolysis do not appear to have attracted the attention they deserve, and very few published papers deal specifically with electrochemical methods of preparation of free radicals and with the characterisation of free radicals thus produced. Yet studies of the properties and behaviour of electrochemically generated free radicals offer great theoretical and practical possibilities.

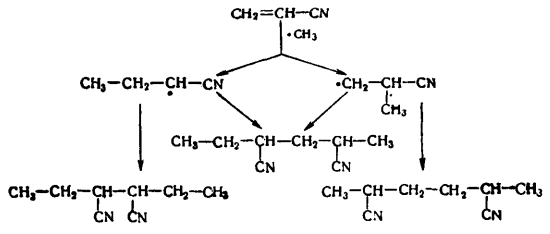
The present article discusses the electrochemical reactions of organic compounds in which free radicals are involved.

2. METHODS OF DETECTING FREE RADICALS IN THE ELECTROLYSIS OF ORGANIC COMPOUNDS

The formation of free radicals during electrolysis of organic compounds can be demonstrated by a number of methods.

One can, for example, make a study of the products which appear when organic compounds are electrolysed in the presence of free radical acceptors, *i.e.*, of unsaturated compounds, which readily combine with free radicals. Styrene, acrylonitrile, butadiene, isoprene, and other similar compounds will readily accept free radicals.

The nature of the free radicals formed during electrolysis can often be inferred from the products obtained when organic compounds are electrolysed in the presence of such acceptors. The method was applied with success to the free radical reactions occurring during the Kolbe synthesis. Thus, electrolysis of a solution of potassium acetate in anhydrous acetic acid containing acrylonitrile gives a number of products [1] whose formation can be described by the following scheme if it is assumed that the anodic process generates methyl radicals which then react with molecules of acrylonitrile:



The electrolysis of sodium acetate solutions in acetic acid containing styrene [1,2], isoprene, or butadiene [3] yields