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Progress in Organic Synthesis Based on 1-Alkoxydienes and 1-Alkoxypolyenes

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This review covers the methods of preparation and chemical properties of 1-alkoxydienes and 1-alkoxypolyenes. The interest in 1-alkoxydienes arises because they form a basis for the easy production of various classes of organic compounds: aliphatic, carbocyclic, and heterocyclic. 1-Alkoxydienes have acquired the greatest importance in the synthesis of polyenes, including natural compounds of the vitamin A and β-carotene type. The higher cyanine dyes have become accessible on the basis of the 1-alkoxydienes.
The review deals with both theoretical and practical aspects of the chemistry of the 1-alkoxydienes and 1-alkoxypolyenes. The review surveys all the information available in world literature on the chemistry of the alkoxydienes and is intended for a wide circle of organic chemists, students, and research students. There is a bibliography of 86 references.

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I. INTRODUCTION

The extremely reactive 1-alkoxydienes, which possess a conjugated diene system and a labile alkoxy-group, are of great interest for synthetic organic chemistry. Studies in recent years have shown that these compounds can be used successfully to obtain aliphatic, carbocyclic, and heterocyclic compounds. However, 1-alkoxydienes are most frequently used for the synthesis of various types of unsaturated compounds, including polyenes belonging to the vitamin A series and carotenoids. The higher cyanines used as dyes also became accessible through the 1-alkoxydienes.

Progress in the field of synthesis and the use of 1-alkoxydienes has still not been surveyed in the chemical literature and the present review has the aim of filling this lacuna. Furthermore this review gives the information, still extremely scanty, about the 1-alkoxypolyenes.

II. SYNTHESIS OF 1-ALKOXY-1,3-DIENES

1. From Acetals of 3-Chlorobutyraldehyde

1-Alkoxy-1,3-dienes were first obtained by Wichterle[1] by heating dialkylacetals of 3-chlorobutyraldehyde with powdered potassium hydroxide; dehydrochlorination occurred with the simultaneous loss of alcohol:

$$CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2CH(OR)_2 \xrightarrow{KOH} CH_2=CH-CH=CHOR + ROH + HCl$$

where R = C_2H_5, n-C_3H_7, n-C_4H_9, iso-C_4H_9.

However, in this method of synthesis the yields of 1-alkoxydienes are very low (~10%) and poorly reproducible. Acetals of crotonaldehyde are usually formed exclusively instead of dienes[2]. Since alkoxydienes could not be obtained by this method in much later investigation[3] it must generally be taken as unsatisfactory.

2. From Ethynyl Vinyl Ethers

Shostakovskii and coworkers[4,5] proposed a method for obtaining 1-alkoxydienes by the partial hydrogenation of ethynyl vinyl ethers over a palladium catalyst. The initial ethers were obtained by the addition of alcohols to diacetylene:

$$CH\equiv C-C\equiv CH + ROH \rightarrow CH\equiv C-CH=CHOR \xrightarrow[Pd]{H_2} CH_2=CH-CH=CHOR,$$

where R = C_4H_9, C_6H_{11}, $C_{10}H_{17}$.

This method was also used for the synthesis of 4-substituted 1-alkoxydiene[6]:

$$C_3H_7-C\equiv C-CH=CHOC_2H_5 \xrightarrow[Pd]{H_2} C_3H_7CH=CH-CH=CHOC_2H_5.$$

3. From Vinylacetylene

Wichterle and Prochazka[7] obtained 1-ethoxybuta-1,3-diene by heating vinylacetylene and alcohol with alkali in an autoclave:

$$CH_2=CH-C\equiv CH + ROH \rightarrow CH_2=CH-CH=CH-OR.$$

According to Treibs[8,9], 1-alkoxybutadiene can be obtained by the addition of aliphatic or cycloaliphatic alcohols to vinylacetylene in the presence of alkali metal alkoxides.

In the production of diacetylene from 1,4-dichlorobutyne and potassium hydroxide solution in methanol Shostakovskii and Khomenko[10] observed the formation of a little 3-chloro-1-methoxybuta-1,3-diene together with other compounds:

$$ClCH_2-C\equiv C-CH_2Cl \rightarrow \left[CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-\underset{\displaystyle Cl}{\underset{|}{C}}=CH_2\right] \rightarrow CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-C\equiv CH \xrightarrow[KOH]{CH_3OH} CH_2=\underset{\displaystyle Cl}{\underset{|}{C}}-CH=CHOCH_3.$$

4. From Acetals of αβ-Unsaturated Aldehydes

Flaig[11] showed that 1-methoxy- and 1-ethoxy-butadiene are readily formed on passing the vapour of the corresponding acetals of crotonaldehyde over contact catalysts

such as NaH_2PO_4, $Al_2(SO_4)_3$, $MgSO_4$, or B_2O_3, at 300–350°C and reduced pressure.

In this way Nazarov and coworkers[12] succeeded in obtaining 1-methoxy- and 1-ethoxy-3-methylbutadiene from acetals of dimethylacrylaldehyde. 1-Butoxy- and 1-hexoxy-butadienes were obtained analogously[13] using Al_2O_3 as catalyst.

Nazarov and coworkers[14] developed a method for obtaining 1-alkoxydienes by the liquid-phase pyrolysis of acetals of $\alpha\beta$-unsaturated aldehydes, for example:

$$CH_3-\underset{\displaystyle R^1}{\underset{|}{C}}=CH-CH(OR)_2 \rightarrow CH_2=\underset{\displaystyle R^1}{\underset{|}{C}}-CH=CHOR,$$

where $R^1 = H$, CH_3.

This method consisted in heating acetals of $\alpha\beta$-unsaturated aldehydes at 165–220°C in the presence of catalysts of the acid type. The process goes in such a manner that the low-boiling alcohols and 1-alkoxydiene formed during the pyrolysis are continuously removed from the reaction zone.

5. From Acetals of Vinylacetaldehyde

A convenient method for obtaining 1-alkoxybutadienes is the pyrolysis of acetals of vinylacetaldehyde[15,16], which can be obtained readily by the condensation of alkyl vinyl ethers in the presence of the complex catalysts $BF_3.O(C_2H_5)_2$ + $Hg(OCOCH_3)_2$ or $BF_3.O(C_2H_5)_2$ + HgO:[15,17]

$$2CH_2=CHOR \xrightarrow[Hg(OCOCH_3)_2]{BF_3\cdot O(C_2H_5)_2} CH_2=CH-CH_2CH(OR)_2 \rightarrow CH_2=CH-CH=CHOR,$$

where $R = C_2H_5$, n-C_4H_9, iso-C_5H_{11}.

The alcohol is removed at 330–350°C in the presence of the catalysts $MgHPO_4.Na_2SiO_3$ [15] or $BaO.SiO_2$,[16] the yield of the dienes being > 70%.

6. From 1,1,3-Trialkoxyalkanes

The most general and convenient method for obtaining 1-alkoxydienes is the pyrolysis of 1,1,3-trialkoxyalkanes:

$$R^1CH_2-\underset{\displaystyle OR}{\underset{|}{CR^2}}-CHR^3-CH(OR)_2 \rightarrow \underset{\displaystyle R^1}{\underset{|}{CH}}=\underset{\displaystyle R^2}{\underset{|}{C}}-\underset{\displaystyle R^3}{\underset{|}{C}}=CHOR + 2ROH.$$

This method allows 1-alkoxydienes with various substituents, both in the diene part and in the alkoxy-residue, to be synthesised in high yield[11,12,14,18–24] (see Table 1).

The initial 1,1,3-trialkoxyalkanes are readily obtained by the condensation of acetals and ketals with alkyl vinyl ethers in the presence of aprotic acids[25,26]:

$$R^1CH_2-CR^2(OR)_2 + R^3-CH=CHOR \xrightarrow{BF_3\cdot O(C_2H_5)_2} R^1CH_2-\underset{\displaystyle OR}{\underset{|}{CR^2}}-CHR^3-CH(OR)_2.$$

This method of synthesis of the 1,1,3-trialkoxyalkanes acquired real practical importance in connection with the development of a practicable method of obtaining ketals and acetals with the aid of tetra-alkoxysilanes[28]. Of the other methods of synthesis of the initial compounds mention must be made of a convenient way of obtaining 1,1,3-trialkoxybutanes from crotonaldehyde and an alcohol[17]:

$$CH_3CH=CH-CHO + ROH \xrightarrow{HCl} CH_3-\underset{\displaystyle OR}{\underset{|}{CH}}-CH_2-CH(OR)_2.$$

The exchange of the alkoxy-groups of 1,1,3-trimethoxy- and 1,1,3-triethoxy-alkanes with higher alcohols allows trialkoxy-compounds with other alkoxy-residues to be obtained easily. Such trialkoxy-derivatives are the starting substances for the synthesis of 1-alkoxydienes with heavy alkoxy-groups[27]:

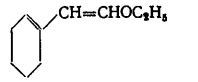
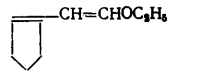
$$CH_3CR^1(OR)-CHR^2-CH(OR)_2 \underset{-2ROH}{\overset{+2R^3OH}{\longrightarrow}} CH_3CR^1(OR^3)-CHR^2-CH(OR^3)_2.$$

The production of 1-alkoxydienes by the pyrolysis of 1,1,3-trialkoxyalkanes is carried out in two ways: vapour-phase and liquid-phase.

In the vapour-phase method for the production of 1-alkoxydienes the vapour of trialkoxyalkanes is passed at reduced pressure over a catalyst at 300–350°C. The catalysts which are used include: $BaO.4SiO_2$ or $BaO.5SiO_2$; $Al_2(SO_4)_3$, $MgSO_4$, NaH_2PO_4, B_2O_3, SiO_2, $MgHPO_4$, and $AlPO_4$.[11,12,14,15,22,27]

It has been shown[12,14,22,29] that the best yields of 1-alkoxydienes are obtained by using $MgHPO_4$ and this catalyst lasts longest.

Table 1. Yields of 1-alkoxydienes in the pyrolysis of 1,1,3-trialkoxyalkanes.

1-Alkoxydiene	Yield, %		Reference
	vapour-phase process	liquid-phase process	
$CH_2=CH-CH=CHOCH_3$	64.0	—	11,12
$CH_2=CH-CH=CHOC_2H_5$	72.0	77.5	11,12,13
$CH_2=CH-CH=CHOC_4H_9$-n	42.0	—	27
$CH_2=CH-CH=CHOC_5H_{11}$-iso	37.0	—	27
$CH_2=CH-CH=CHOC_8H_{17}$-n	43.0	—	27
$CH_3CH=CH-CH=CHOC_2H_5$	71.5	65.0	14,24
$CH_2=C(CH_3)-CH=CH-OCH_3$	71.0	—	12
$CH_2=C(CH_3)-CH=CH-OC_2H_5$	77.0	64.0	12,14,23–24
$CH_2=C(CH_3)-CH=CH-OC_4H_9$-n	51.5	52.0	14,27
$CH_2=C(CH_3)-CH=CH-OC_5H_{11}$-iso	—	43.5	27
$CH_2=CH-(CH_3)C=CHOC_2H_5$	62.0	68.3	14,24
$CH_2=CH-(CH_3)C=CHOC_5H_{11}$-iso	41.0	—	27
$C_2H_5CH=CH-CH=CHOC_2H_5$	—	68.6	14
$(CH_3)_2C=CH-CH=CHOC_2H_5$	—	77.8	14
$CH_2=C(CH_3)-C(CH_3)=CHOC_2H_5$	—	65.0	14,24
$CH_3-CH=CH-C(CH_3)=CHOC_2H_5$	—	59.0	14,24
	75.4	82.0	14
	—	83.2	14

The liquid-phase pyrolysis of 1,1,3-trialkoxyalkanes is carried out just as for the acetals of $\alpha\beta$-unsaturated aldehydes (see above). NaH_2PO_4, $NH_4H_2PO_4$, p-toluenesulphonic acid[29], and p-toluenesulphonic acid–quinoline mixture[23,24] have been used as catalysts[14,21], the best being $NH_4H_2PO_4$ and p-$CH_3C_6H_4SO_3H$–quinoline.

It should be noted that when a mixture of p-toluenesulphonic acid and quinoline is used as catalyst the pyrolysis of alkoxyalkanes with a terminal isoprenyl group $CH_2=C(CH_3)-$, rearrangement is observed, with the formation of 1-alkoxydienes with an n-propenyl structure $CH_3-CH=CH-$, the content of which in the reaction products reaches 10–20%:[30]

$$CH_2=\underset{\displaystyle CH_3}{\underset{|}{C}}-\underset{\displaystyle R}{\underset{|}{C}}=CH-OC_2H_5 \rightarrow CH_3CH=CH-\underset{\displaystyle R}{\underset{|}{C}}=CHOC_2H_5$$

where R = H, CH_3.

7. From Phosphonates of γ-Vinyl Ethers and Carbonyl Compounds (According to Khorner)

In this method the phosphonates of γ-vinyl ethers, which can be obtained by the pyrolysis of the acetals of γ-carbonylphosphonates, react with carbonyl compounds in the presence of a base (sodium hydride) in a medium of hexamethylphosphotriamide[31]. As a result 1-alkoxydienes are formed:

$$(RO)_2\underset{\displaystyle O}{\underset{\downarrow}{P}}-CH_2CH_2-\underset{\displaystyle R^1}{\underset{|}{C}}(OC_2H_5)_2 \rightarrow (RO)_2\underset{\displaystyle O}{\underset{\downarrow}{P}}-CH_2-CH=\underset{\displaystyle R^1}{\underset{|}{C}}-OC_2H_5$$

$$\xrightarrow{O=CR^2R^3} R^2R^3C=CH-CH=CR^1-OC_2H_5.$$

This method is extremely laborious and the initial compounds are not readily available; however, it allowed 1-ethoxydienes with structures which could not be made by other methods to be obtained. Table 2 gives the yields of the 1-ethoxydienes obtained by this method[31].

Table 2. Yields of 1-alkoxydienes after Sturtz and Lavielle[31].

Ethoxydiene	Yield %	Ethoxydiene	Yield %
$(C_6H_5)_2C{=}CH{-}CH{=}CHOC_2H_5$	68	cyclo-$C_6H_{10}{=}CH{-}CH{=}CHOC_2H_5$	37
$C_6H_5CH{=}CH{-}CH{=}CHOC_2H_5$	48	$(C_6H_5)_2C{=}CH{-}CH{=}C(CH_3){-}OC_2H_5$	40
p-$CH_3OC_6H_4{-}CH{=}CH{-}CH{=}CHOC_2H_5$	47	p-$CH_3OC_6H_4CH{=}CHCH{=}C{-}OC_2H_5$	40
p-$(CH_3)_2NC_6H_4CH{=}CH{-}CH{=}CHOC_2H_5$	48	CH_3	
$(CH_3)_2CH{-}CH{=}CH{-}CH{=}CHOC_2H_5$	57		
$C_2H_5{-}C(CH_3){=}CH{-}CH{=}CHOC_2H_5$	33	cyclo-$C_6H_{10}{=}CH{-}CH{=}C(CH_3){-}OC_2H_5$	40

8. Geometrical Isomerism of 1-Alkoxydienes

The problem of the geometric isomerism of 1-alkoxydienes has been repeatedly mentioned in the literature but a conclusive solution has not yet been obtained.

In 1950 Farmilo and Nichols[20] reported that in the pyrolysis of 1,1,3-trimethoxybutane isomeric *cis*- and *trans*-1-methoxybutadienes are formed, the proportion of the *cis*-isomer being ~ 60%. Their conclusion that *cis*–*trans* isomerism existed in the reaction products was based on the fact that in the reaction with maleic anhydride an addition product corresponding to the *trans*-isomer is readily formed, whereas under these conditions the *cis*-isomer evidently does not give an adduct with maleic anhydride, but polymerises.

In 1964 Štěpek[32] studied the problem of the existence of geometric isomers of 1-methoxybutadiene, but despite extreme care could not isolate *cis*- and *trans*-isomers. On the other hand, kinetic investigations of the reaction of 1-methoxybutadiene with maleic anhydride showed that this reaction actually proceeds in two directions—diene synthesis and copolymerisation—however, this is explained not by the existence of stable *cis*- and *trans*-isomers, as has been suggested[20], but signifies that two parallel reactions with different mechanisms occur. Copolymerisation proceeds by a radical mechanism, whereas the diene addition is not affected by either radical initiators or inhibitors. In this connection Štěpek assumes that Farmilo and Nichols[20] erroneously took to be the *cis*-isomer of 1-methoxybutadiene a certain amount of the dimethylacetal of crotonaldehyde, which is obtained in the synthesis of 1-methoxybutadiene.

In 1967 it was shown[33], with the aid of infrared spectroscopy and gas-liquid chromatography that the 1-methoxybutadiene obtained by the loss of alcohol from 1,1,3-trimethoxybutane in the presence of phosphoric acid as catalyst[34] is the pure *trans*-isomer.

However, Martin and coworkers[35], who employed semi-preparative gas–liquid chromatography succeeded in isolating small quantities of a strongly enriched mixture and in some instances, the pure *cis*- and *trans*-isomers of 1-ethoxy-1,3-dienes

$$R{-}CH{=}C(R^1){-}C(R^2){=}CHOC_2H_5,$$

(where R, R^1, and R^2 = H, CH_3) and of identifying them by the NMR method. Furthermore, the NMR method was used to study the relative stability of compounds unsubstituted at the end of the chain (R = H) and to determine the equilibrium constants of the *cis*–*trans* isomerisation. On the basis of the results obtained it was concluded that the *trans*-1,2-isomer is always more stable than the *cis*-1,2-isomer and substitution at the double bond increases the stability of the *cis*-1,2-configuration.

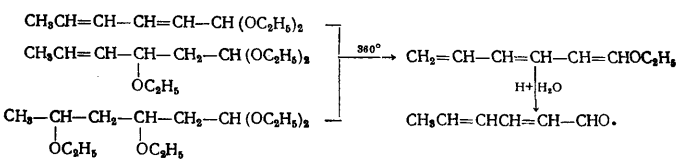
The ultraviolet and infrared spectra of the 1-alkoxydienes, both unsubstituted and with various substituents in the chain, have been investigated[27]. All the 1-alkoxydienes have an absorption band in the 235–247 nm range (in heptane), displaced considerably to longer wavelengths in comparison with the absorption band of butadiene (~ 217 nm [36]).

In the infrared spectra the frequency of the stretching vibrations of the C–C bond of the 1-alkoxydienes lies in the same range as for the alkyl derivatives of butadiene (~ 1650 cm^{-1}); splitting of the lines of the C–C bond is sometimes observed.

III. SYNTHESIS OF 1-ALKOXYPOLYENES

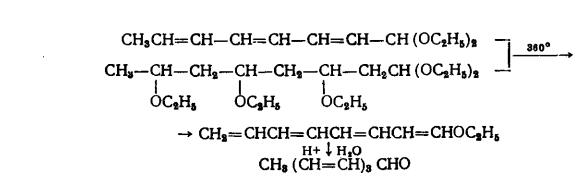
1-Alkoxypolyenes, like 1-alkoxydienes, are vinylogues of the simple vinyl ethers. Makin and Sudakova[37] showed that the pyrolysis of acetals and alkoxyacetals is universal and can be used with success not only for the synthesis of simple vinyl and diene ethers but also for the synthesis of 1-alkoxypolyenes.

In the vapour-phase pyrolysis of the acetal of 2,4-hexadienaldehyde and also of 1,1,3-triethoxyhex-4-ene over $MgHPO_4$, Na_2SiO_3 as catalyst at 360°C and reduced pressure, 1-ethoxyhexa-1,3,5-triene is formed in > 70% yield:



The structure of 1-ethoxyhexa-1,3,5-triene was confirmed by the presence in the ultraviolet spectrum of an absorption maximum at 272 nm (in heptane), which is characteristic for three conjugated bonds. In the hydrolysis of 1-ethoxyhexatriene by a dilute solution of sulphuric acid, hexa-2,4-dienaldehyde is formed. 1-Ethoxyhexa-1,3,5-triene is readily polymerised in air but in nitrogen at 0°C it can be kept for several months.

Similarly, 1-ethoxyocta-1,3,5,7-tetraene was obtained in 49–54% yield by the pyrolysis of either octatrienal acetal or 1,1,3,5,7-pentaethoxyoctane over acid phosphates[37]:



1-Ethoxytetraene is unstable and is converted into octa-2,4,6-trienal on hydrolysis in acid.

IV. SYNTHESIS ON THE BASIS OF 1-ALKOXY-1,3-DIENES

1. Hydrogenation

The exhaustive hydrogenation of 1-alkoxydienes in the presence of platinum black, $Pd/CaCO_3$, or nickel catalysts leads to ethers[33,38]. Thus butyl methyl, ethyl isopentyl, and butyl isopentyl ethers were obtained from 1-methoxybuta-1,3-diene, 1-ethoxy-3-methylbuta-1,3-diene, and 1-butoxy-3-methylbuta-1,3-diene respectively. The partial hydrogenation of 1-alkoxydienes does not take place selectively, but with the formation of a mixture of isomeric compounds[33,39], as is shown in the scheme. The addition of 1 mole hydrogen to *trans*-1-methoxybuta-1,3-diene gives a mixture of all possible hydrogenation products[33]:

$$CH_2{=}CHCH{=}CHOCH_3 + H_2 \rightarrow \underset{\text{1,2- addition}}{CH_2{=}CHCH_2CH_2OCH_3} +$$
$$+ \underset{\text{1,4- addition cis- and trans-}}{CH_3CH{=}CHCH_2OCH_3} + \underset{\text{3,4- addition cis and trans-}}{CH_3CH_2CH{=}CHOCH_3} + \underset{\text{complete hydrogenation}}{C_4H_9OCH_3}$$

In the presence of platinum black and especially palladium catalyst the main product is *trans*-1-methoxybut-1-ene (3,4-addition). Partial hydrogenation in the presence of Raney nickel catalyst gives almost equal amounts of the products of 1,2-, 3,4-, and 1,4-addition.

2. Hydrolysis

The hydrolysis of 1-alkoxydienes under the action of 2% sulphuric acid leads $\alpha\beta$-unsaturated aldehydes[38]:

$$R{-}CH{=}\overset{R^1}{\overset{|}{C}}{-}CH{=}CHOC_2H_5 \xrightarrow[H^+]{H_2O} RCH_2{-}\overset{R^1}{\overset{|}{C}}{=}CH{-}CHO$$

where R, R^1 = H, CH_3.

In this way crotonaldehyde, 3-methylcrotonaldehyde, and 4-methylcrotonaldehyde were obtained in good yield from 1-ethoxybuta-1,3-diene, 1-ethoxy-3-methylbuta-1,3-diene, and 1-ethoxypenta-1,3-diene respectively. Probably the addition of water to 1-alkoxydienes occurs in the 1,4-position of the diene system, although it is difficult to draw definite conclusions since $\beta\gamma$-unsaturated aldehydes (obtained when there is 1,2-addition) readily rearrange in acid medium into $\alpha\beta$-unsaturated aldehydes.

3. Addition of [Substituted] Silanes

It was shown recently that 1-alkoxydienes are capable of adding silane derivatives[40]. The addition of fluoromethylpropylsilanes to a diene ether takes place in the presence of hydrogen hexachloroplatinate(IV) with the formation of 1-butoxy-4-(fluoromethylpropylsilyl)but-1-ene with yields of up to 91%; an addition product with two molecules of the silane is liberated in small amounts:

$$C_4H_9OCH{=}CH{-}CH{=}CH_2 + HSiRR'F \begin{cases} \rightarrow C_4H_9OCH{=}CHCH_2CH_2SiRR'F \\ \rightarrow C_4H_9OCH_2CH(SiRR'F){-}CH_2CH_2SiRR'F. \end{cases}$$

Here we encounter a rare instance of addition to 1-alkoxydienes in the 1,2- and 3,4-positions.

The reaction of methyldichlorosilane with 1-butoxybuta-1,3-diene is accompanied by resinification of the ether and the addition product could be isolated only in 1.2% yield.

4. Addition of Alchols

1-Alkoxy-1,3-dienes add alcohols even in the cold or at room temperature in the presence of catalytic amounts of hydrochloric acid, acetals of $\alpha\beta$-unsaturated aldehydes being obtained in good yield[14,38,41]:

$$CH_2{=}\overset{R^1}{\overset{|}{C}}{-}CH{=}CHOR + ROH \xrightarrow{H^+} CH_2{-}\overset{R^1}{\overset{|}{C}}{=}CH{-}CH(OR)_2$$

where R^1 = H, CH_3; R = CH_3, C_2H_5, n-C_4H_9, iso-C_5H_{11}.

The structure of the reaction products was shown by countersyntheses and infrared spectroscopy[38].

The diethyl-, dibutyl-, and di-isopentyl-acetals of crotonaldehyde were obtained in this way from 1-ethoxy-, 1-butoxy-, and 1-isopentyloxy-butadiene respectively[38,41] and the diethyl- and dibutyl-acetals of 3-methylcrotonaldehyde were obtained from ethoxy- and butoxy-isoprene[14,38].

Kubler[42], having studied the addition of methanol to 1-methoxybutadiene and of ethanol to 1-ethoxybutadiene in the presence of sulphuric acid, states that this reaction is accompanied by the formation of 1,1,5-trialkoxyocta-2,6-dienes by the scheme:

$$CH_2{=}CH{-}CH{=}CHOCH_3 + H^+ \rightarrow CH_3CH{=}CH{-}\overset{+}{C}HOCH_3 \rightarrow$$
$$\xrightarrow{CH_2=CH-CH=CHOCH_3} CH_3CH{=}CHCH(OCH_3)CH_2CH{=}\overset{+}{C}HOCH_3 \rightarrow$$
$$\xrightarrow{CH_3OH} CH_3CH{=}CH{-}CH(OCH_3)CH_2CH{=}CH(OCH_3)_2 + H^+.$$

It should be noted that the addition of alcohols to 1-alkoxydienes can serve as a preparative method for obtaining difficultly accessible acetals from $\alpha\beta$-unsaturated aldehydes.

5. Bromination and Bromoalkoxylation

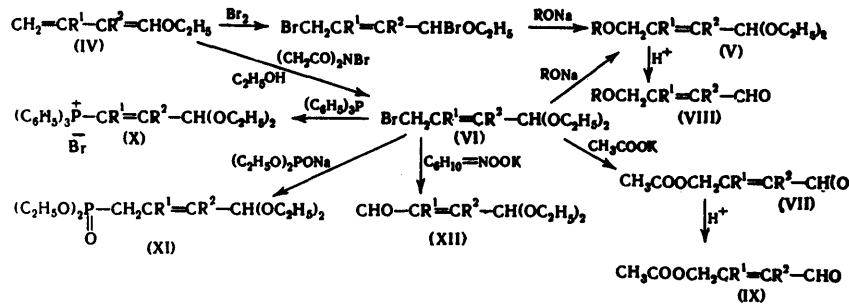
1-Ethoxybutadiene adds the first bromine molecule in the 1,4-position of the diene system. In further bromination a second bromine molecule is added with the formation of a crystalline tetrabromide[11]:

$$CH_2{=}CH{-}CH{=}CHOC_2H_5 \xrightarrow{Br_2} CH_2{-}\underset{Br}{CH}{=}CH{-}\underset{Br}{CH}OC_2H_5 \xrightarrow{Br_2}$$
$$\rightarrow \underset{(I)}{CH_2{-}\underset{Br}{CH}{-}\underset{Br}{CH}{-}\underset{Br}{CH}OC_2H_5}.$$

Both the dibromide (I) and, in particular, the tetrabromide are very unstable compounds. On treating dibromide (I) with sodium ethoxide it is converted into an acetal of 4-ethoxycrotonaldehyde (II) and the loss of alcohol from (II) yielded 1,4-diethoxybuta-1,3-diene (III):[11]

$$(I) \xrightarrow{2C_2H_5ONa} \underset{(II)}{C_2H_5OCH_2CH{=}CH(OC_2H_5)} \xrightarrow[Al_2O_3]{350^\circ} \underset{(III)}{C_2H_5OCH{=}CHCH{=}CHOC_2H_5}.$$

The bromination of substituted 1-alkoxydienes (IV) has been studied[38], and the direction of the reaction and structure of the bromides obtained was established from the products of their reaction with alkoxides. The formation of acetals of $\alpha\beta$-unsaturated γ-alkoxyaldehydes (V) shows that the addition of bromine occurs in the 1,4-position.



where R = CH_3, C_2H_5; R^1 and R^2 = H, CH_3.

The bromoalkoxylation of 1-alkoxydienes (IV) is extremely interesting and promising. This reaction, which takes place on the treatment of 1-alkoxydienes with bromosuccinimide in alcoholic medium leads to acetals of $\alpha\beta$-unsaturated 4-bromoaldehydes (VI).[11,38] Using the high reactivity of allyl bromide, various difficultly accessible bifunctional derivatives of $\alpha\beta$-unsaturated aldehydes[38] were readily obtained, a route of wide use in organic synthesis. The bromoalkoxylation of 1-ethoxybuta-1,3-diene[11,38], 1-ethoxy-2-methylbuta-1,3-diene[38], and 1-ethoxy-3-methylbuta-1,3-diene[38] was investigated.

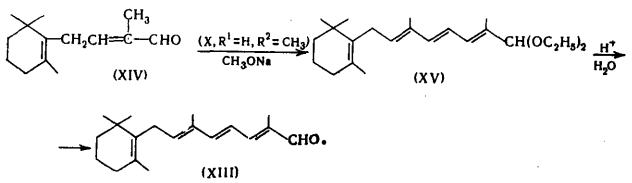
The reaction of 4-bromoacetals (VI) with alkoxides or potassium acetate gave in good yield the acetals of γ-alkoxy- (V) and γ-acetoxy- (VII) derivatives of $\alpha\beta$-unsaturated aldehydes respectively. In the hydrolysis by dilute phosphoric acid, (V) and (VII) are readily converted into the corresponding γ-alkoxy- (VIII) and γ-acetoxy- (IX) substituted $\alpha\beta$-unsaturated aldehydes[38].

γ-Bromoacetals (VI) react readily with triphenylphosphine with the formation of phosphonium salts[29,43-45] (X), and on reaction with sodium diethyl phosphite they are converted into phosphonates (XI).[29]

The bromomethyl group in 4-bromoacetals (VI) can be oxidised to an aldehyde group by reaction with the potassium salt of nitrocyclohexane[38,46,47]. This provides a possible route to the previously difficultly accessible monoacetals of fumaraldehyde and its alkylsubstituted derivatives (XII).

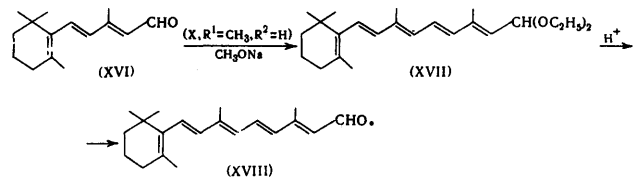
The bifunctional derivatives of $\alpha\beta$-unsaturated aldehydes obtained on the basis of 1-alkoxydienes were used for the synthesis of polyene compounds of various types and principally for the synthesis of derivatives of vitamin A and carotenoid precursors.

Thus, 1-ethoxy-2-methylbutadiene was used for obtaining β-C_{19}-aldehyde (XIII)[44], which is a key product in the synthesis of β-carotene:

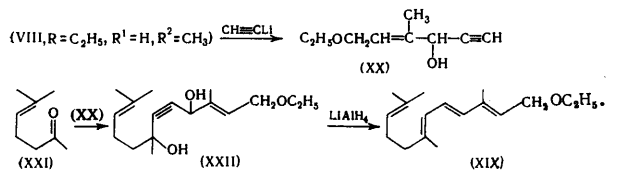


Here the reaction of the phosphonium salt (X; R^1 = H, R^2 = CH_3) with β-C_{14} aldehyde (XIV) in the presence of sodium methoxide gave an acetal of β-C_{19} aldehyde (XV), hydrolysis of which by dilute phosphoric acid gave quantitatively a mixture of the *cis–trans*-isomers of β-C_{19} aldehyde (XIII).

Similarly, reaction of β-ionolydeneacetaldehyde (XVI) with a phosphonium salt (X; R^1 = CH_3, R^2 = H) obtained from 1-ethoxy-3-methylbutadiene, gave the acetal of the aldehyde of vitamin A (XVII), which forms on acid hydrolysis the aldehyde of vitamin A (XVIII)[45]:

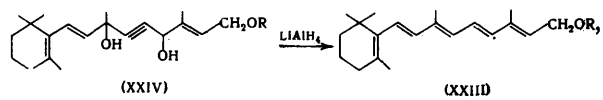


Several synthetic routes to the polyene ethers of isoprenoid structure (including ethers of vitamin A) have been proposed on the basis of 1-alkoxydienes. The scheme given below shows the synthesis of the ethyl ether of dehydrofarnesol (XIX)[48]:



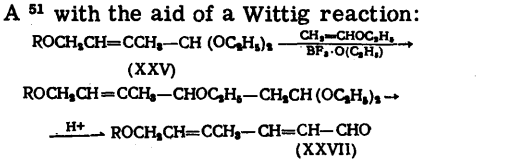
In this synthesis the condensation of 1-ethoxy-3-methylhex-2-en-5-yn-4-ol (XX) with methylheptenone (XXI) gave the acetylenic glycol (XXII), which on reaction with lithium tetrahydroaluminate was converted into the ethyl ether of dehydrofarnesol (XIX) (the Nayler–Whiting reaction[49]).

This reaction was subsequently used to obtain the ethyl ether of vitamin A (XXIII):[50]



where R = C_2H_5. The initial acetylenic glycol (XXIV) was obtained by two paths: (1) by condensation of β-ionone with the Iotsich complex obtained from (XX), and (2) from ethynyl-β-ionol and γ-ethoxytiglinaldehyde (VIII; R = C_2H_5, R^1 = H, R^2 = CH_3).

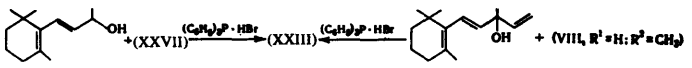
γ-Alkoxy- and γ-acetoxy-tiglinaldehydes and their acetals obtained from the corresponding 1-alkoxydienes open yet another synthetic route to the esters and ethers of vitamin A[51] with the aid of a Wittig reaction:



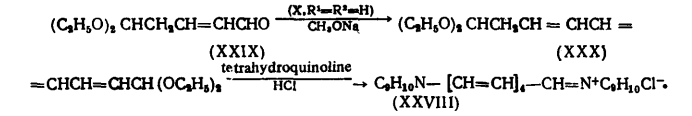
where R = CH_3, $COCH_3$.

The acetals of γ-methoxy- and γ-acetoxytiglinaldehyde (XXV) readily condense with ethyl vinyl ether with the formation of the corresponding 1,1,3-trialkoxy-compounds (XXVI), which on heating with acetic acid are converted

into ω-substituted hexadienals (XXVII). Ethers of vitamin A (XXIII; R = CH_3, $COCH_3$) were synthesised[51] subsequently, as is shown by the scheme:



The reactions of 1-alkoxydienes considered above can be used successfully for the synthesis of cyanines. Thus the acetal of γ-bromocrotonaldehyde, obtained from 1-ethoxybutadiene, was used for making the cyanine (XXVIII)—an intermediate in the synthesis of pentacarbocyanine sensitisers[29,52]:

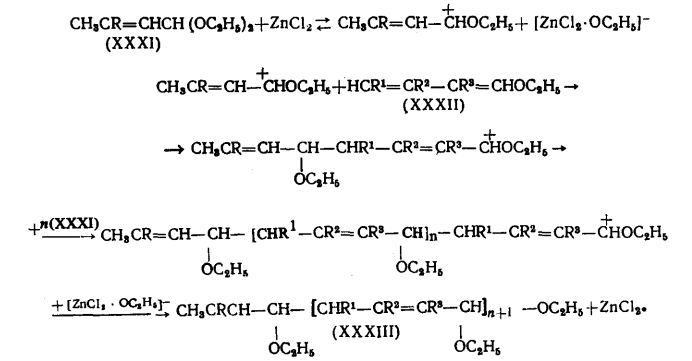


Here the condensation of 5,5-diethoxypent-2-enal[52,53] (XXIX) with 4-(1,1-diethoxybut-2-enyl)triphenylphosphonium bromide (X; $R^1 = R^2 = H$) in the presence of sodium methoxide gives nonatriendial tetraethyl acetal (XXX), which on treatment with tetrahydroquinoline in hydrochloric acid is readily converted into (XXVIII).

6. Condensation with Acetals of $\alpha\beta$-Unsaturated Aldehydes

Nazarov and Krasnaya showed[54,55] that 1-alkoxydienes, like alkyl vinyl ethers, readily condense with the acetals of $\alpha\beta$-unsaturated aldehydes in the presence of aprotic acids —$ZnCl_2$, $BF_3.O(C_2H_5)_2$, etc. For example, it was shown that in the condensation of the acetals of crotonaldehyde and β-methylcrotonaldehyde with 1-ethoxybuta-1,3-diene, 1-ethoxy-3-methylbuta-1,3-diene[54,55], 1-ethoxy-2-methylbuta-1,3-diene[56], 1-ethoxypenta-1,3-diene[57], and 1-ethoxy-2,3-dimethylbuta-1,3-diene[56], the addition of acetals to 1-alkoxydienes, whether substituted or unsubstituted, takes place in the 1,4-position of the diene system of the 1-alkoxydiene.

The addition of acetals (XXXI) to 1-alkoxydienes (XXXII) yields new acetals of $\alpha\beta$-unsaturated aldehydes, which in their turn are also capable of addition to 1-alkoxydienes so that a mixture of the first, second, third, and other successive addition products (XXXIII) is obtained, readily separable by fractional distillation. The mechanism of this condensation is as follows[56]:



Hence the addition of acetals to 1-alkoxydienes has the character of telomerisation, the extent of which depends on the ratio of the acetal and alkoxydiene taken in the reaction.

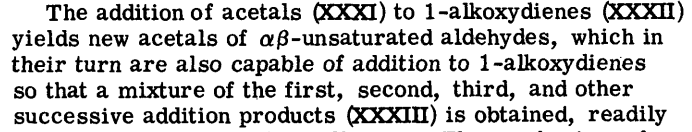
The example of the condensation of crotonaldehyde acetal with 1-ethoxypenta-1,3-diene was used[57] to investigate the dependence of the composition of the telomeric products on the ratio of the acetal to 1-alkoxydiene; the results are given in Table 3.

Table 3 shows that a change in the alkoxydiene : acetal ratio allows the course of the reaction to be regulated to some extent, by directing it to the side of the preferential formation of the desired product. A similar picture is also observed for other 1-alkoxydienes and acetals. The reaction examined is a comparatively simple method of growing a chain of 4, 8, 12, or 16 carbon atoms at one stroke.

Table 3. Telomerisation[57] of acetals of crotonaldehyde with 1-ethoxypenta-1,3-dienes.

Alkoxydiene : acetal ratio	Yield of telomer (XXXIII $R' = CH_3$, $R = R^2 = R^3 = H$)				
	$n=0$	$n=1$	$n=2$	$n=3$	total
1:2	48	30	12	3	93
2:3	28	41	16.5	5	90.5
1:1	27	12	37	8.5	84.5
2:1	9.5	6	26	26.5	68

A remarkable property of alkoxyacetals (XXXIII) was that on heating with 90% acetic acid they are converted in high yield into polyene aldehydes (XXXIV) and on heating with dilute phosphoric acid are hydrolysed with quantitative formation of alkoxyaldehydes (XXXV) which under the action of p-toluenesulphonic acid in toluene are also readily converted into polyenals (XXXIV)[54-57].

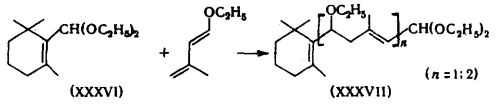


where R, R^1, R^2, R^3 = H, CH_3; n = 0, 1, 2.

The condensation of acetals of $\alpha\beta$-unsaturated aldehydes with 1-alkoxydienes has made the natural polyenes of the isoprenoid structure extremely accessible.

The conversions considered above were used for the synthesis of β-ionolideneacetaldehyde, the aldehyde of vitamin A, and vitamin A (alcohol).

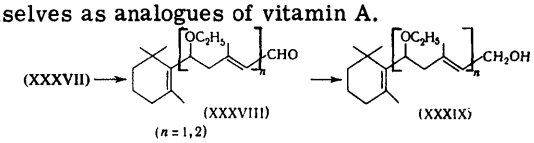
The condensation of β-cyclocitral acetal (XXXVI) with 1-ethoxyisoprene in the presence of zinc chloride as catalyst yielded[58] a mixture of the ethoxyacetals of C_{15} aldehyde (XXXVII; n = 1) and the C_{20} aldehyde (XXXVII; n = 2) with yields of 44.6 and 25% respectively:



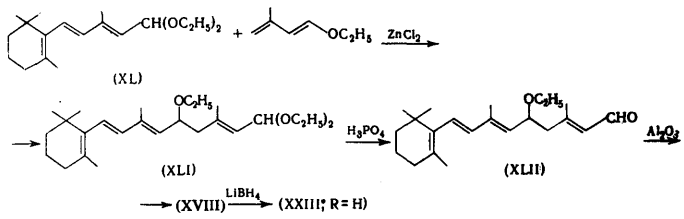
Under the action of orthophosphoric acid in dioxan, (XXXVII; n = 1) is converted into β-ionolideneacetaldehyde (XVI) and on hydrolysis with dilute phosphoric acid,

into ethoxydihydro-β-ionolideneacetaldehyde (XXXVIII, $n = 1$) in good yield. Reduction of (XXXVIII; $n = 1$) with sodium tetrahydroborate gives ethoxydihydro-β-ionolideneethanol (XXXIX; $n = 1$).

In a similar manner, the diethoxybisdihydroaldehyde of vitamin A (XXXVIII; $n = 2$) and diethoxybisdihydrovitamin A (XXXIX; $n = 2$) were obtained in good yield from (XXXVII; $n = 2$). These compounds can be used for the synthesis of vitamin A and in addition they are of interest themselves as analogues of vitamin A.

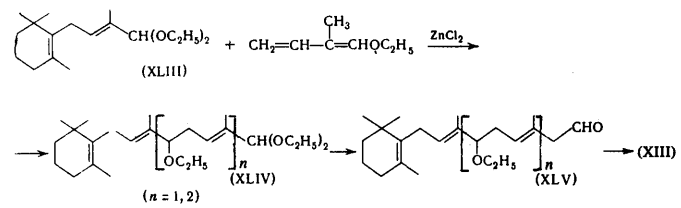


Vitamin A was synthesised by the condensation of β-ionolideneacetaldehyde (XL) with 1-ethoxyisoprene [59,60]. The ethoxyacetal (XLI) thus obtained in 62% yield hydrolyses quantitatively into dihydrovitamin A ethoxyaldehyde (XLII), which on chromatography on aluminium oxide gives the vitamin A aldehyde (XVIII):



On reduction of (XVIII) with lithium tetrahydroborate vitamin A (XXIII, R = H) is obtained.

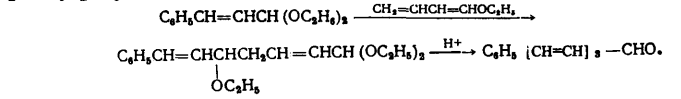
The method described above for growing a polyene chain was used for the synthesis of β-C_{19} aldehyde (XIII) [61].



With this aim the β-C_{19} ethoxyacetal (XLIV; $n = 1$) and β-C_{24}-diethoxyacetal (XLIV; $n = 2$) were obtained by the addition of β-C_{14} aldehyde acetal to 1-ethoxy-2-methylbutadiene. The hydrolysis of these ethoxyacetals with dilute phosphoric acid gives, in quantitative yield, β-C_{19}-ethoxyaldehyde (XLV; $n = 1$) and β-C_{24}-diethoxyaldehyde (XLV; $n = 2$) respectively. Removal of alcohol from (XLV; $n = 1$) led to the fully *trans*-β-C_{19}-aldehyde (XIII).

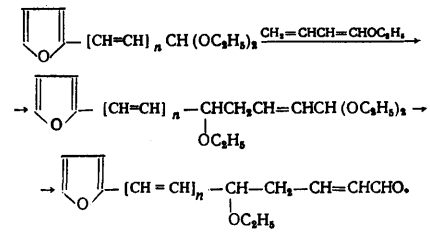
It has been shown [62] that citral acetal is also capable of being condensed with 1-ethoxyisoprene, to form a mixture of telomers of isoprenoid structure.

The condensation of cinnamaldehyde acetal with 1-ethoxybutadiene provided a new method for the production of phenylpolyenes [63]:



In this way the acetals of αβ-unsaturated aldehydes are readily condensed with 1-alkoxydienes. However, there is almost no information about a similar condensation for ketals. The reaction of acetophenone ketal with 1-ethoxybutadiene has been described [64], it being noted that the yield of the condensation product was very low.

Furfural acetal and β-(2-furyl)acrolein acetal readily add to 1-ethoxybutadiene to form normal condensation products [63]:

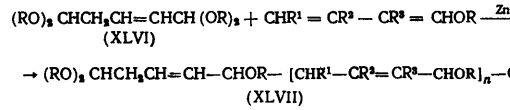


($n = 0$ or 1; yield 40%).

The condensation of 1-alkoxydienes with diacetals of glutaconaldehyde (XLVI) is very interesting, since it allowed previously inaccessible cyanines—the derivatives of higher polyene dialdehydes—to be synthesised simply [29,65-67].

Glutaconaldehyde acetals have two acetal groups, one of which is αβ-unsaturated, the other βγ-unsaturated. It was found experimentally that the condensation of glutaconaldehyde acetal takes place selectively, solely at the αβ-unsaturated acetal group, and the βγ-unsaturated group does not participate in the reaction. This course for the reaction agrees with the theoretical ideas about the mechanism of addition of acetals to alkyl vinyl ethers [68,69].

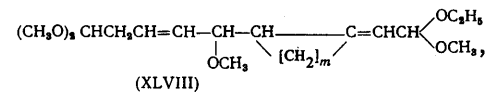
The condensation of glutaconaldehyde acetals [70,71] with 1-methoxybuta-1,3-diene, 1-ethoxypenta-1,3-diene, 1-ethoxy-2-methylbuta-1,3-diene, and 1-ethoxy-3-methylbuta-1,3-diene [29,66] has been studied. In every instance a mixture of telomeric compounds (XLVII), readily separable by fractional distillation, was obtained:



where $n = 1, 2, 3$; R = CH_3, C_2H_5; R^1, R^2, R^3 = H, CH_3.

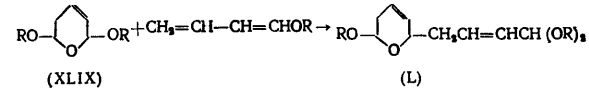
Alkoxyacetals of dialdehydes with 9, 13, and 17 carbon atoms in the chain were obtained according to this scheme.

Derivatives of a dialdehyde with six-membered ($m = 4$) and five-membered ($m = 3$) rings in the chain were obtained in the condensation of glutaconaldehyde acetals with 1-β-(ethoxyvinyl)cyclohexene and 1-β-(ethoxyvinyl)cyclopentene [66]:



where $m = 3$ or 4.

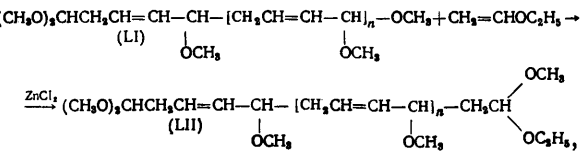
Although 1-alkoxydienes are capable of condensing with 2,6-dialkoxy-Δ^3-dihydropyranes (VLIX) [72] the yield of the condensation product (L) is low (17%) [65]:



where R = CH_3.

In their turn C_9- and C_{13}-alkoxydiacetals (LI; $n = 1$ and 2, respectively), obtained by the condensation of glutaconaldehyde acetal with 1-methoxybutadiene, are capable of reacting with ethyl vinyl ether to form alkoxyacetals

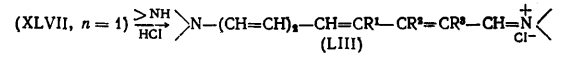
(LII), containing respectively 11 and 15 carbon atoms in the chain. The yield of (LII) is 41–43%:



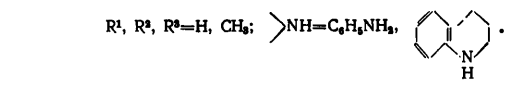
where $n = 1$ or 2.

The condensation examined is a simple general method for the synthesis of alkoxyacetals of unsaturated dialdehydes with 9, 11, 13, 15, or 17 carbon atoms in the chain.

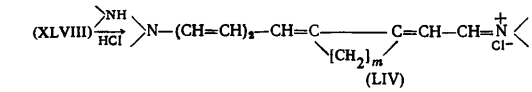
In the acid hydrolysis of the condensation products of glutaconaldehyde with 1-alkoxydienes (XLII; $n = 1$) in the presence of primary or secondary amines a δ-alkoxy-group is lost extremely readily, and cyanines (LIII) are formed in very good yield (up to 80%) [29,67]:



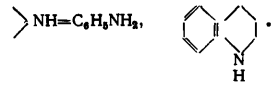
where



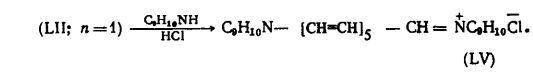
Cyanines (LIV) with six- and five-membered rings respectively in a conjugated chain[29] were obtained from alkoxydiacetals (XLVIII; $m = 4$ and 3)



where $m = 3$ or 4;

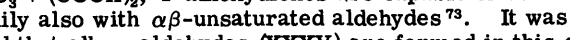


This method for obtaining cyanines was used for the synthesis of undecamethine compounds. Thus in the treatment of 1,3,7,11,11-pentamethoxy-1-ethoxyundeca-4,8-diene (LII; $n = 1$) with tetrahydroquinoline in dilute hydrochloric acid, bistetrahydroquinolide undecatetraenedial chloride [quinolinylundecapentaeneylidene quinolinium chloride] (LV) is formed in good yield[66]:



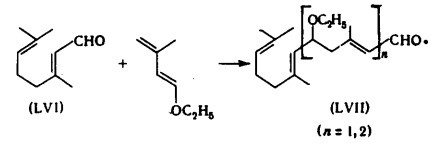
7. Condensation with αβ-Unsaturated Aldehydes

In the presence of catalysts such as BF_3, $ZnCl_2$, and H_3BO_3 + $(COOH)_2$, 1-alkoxydienes are capable of reacting readily also with αβ-unsaturated aldehydes[73]. It was found that alkoxyaldehydes (XXXV) are formed in this condensation:



which are readily converted into polyenals (XXXIV) on heating with phosphoric acid. 5-Ethoxycitral, 5,9-diethoxyfarnesal, octa-2,4,6-trienal, 3-methylocta-2,4,6-trienal, dodeca-2,4,6,8,10-pentaenal, and dehydrocitral were obtained in this way[73].

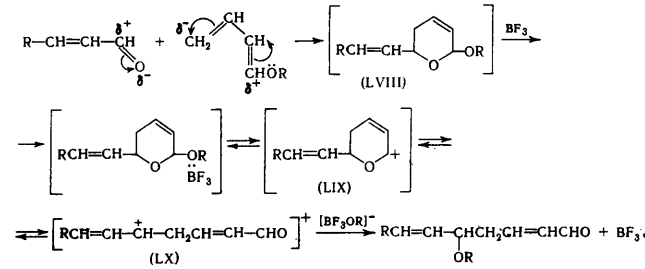
Citral (LVI) is also capable of undergoing this condensation, with the formation of terpene compounds[73] (LVII):



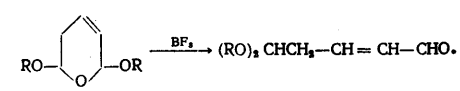
Furfural condenses rather readily with 1-ethoxybutadiene in the presence of the catalysts mentioned above. Here, as in other instances, a mixture of telomeric alkoxyaldehydes is obtained, which are then easily converted into furylpolyenals[73]. Unlike furfural, benzaldehyde condenses with 1-ethoxybutadiene with great difficulty, the yield of condensation product (5-ethoxy-5-phenylpent-2-enal) being ~ 10%.

β-Cyclocitral, 2,3-dihydro-2-methylbenzaldehyde, and also aliphatic aldehydes (butyraldehyde, isovaleraldehyde) seemed to be incapable of undergoing this condensation[73].

From our standpoint it seems most probable that the condensation of unsaturated aldehydes with 1-alkoxydienes is accompanied by the intermediate formation of dihydropyran (LVIII) as a result of a reaction of the diene synthesis type. Furthermore, the action of an acid catalyst, for example, BF_3, on (LVIII) produces an unstable carbonium ion (LIX), which then rearranges into the more stable αβ-unsaturated cation (LX). The reaction of (LX) with $[BF_3OR]^-$ leads to δ-alkoxyaldehydes of the (XXXV) type:



An indirect confirmation of this mechanism is the recent observation[53] of the rearrangement of 2,6-dialkoxy-Δ³-dihydropyrans into glutaconaldehyde monoacetal:



8. Reaction with Formylating Agents

In the reaction of 1-alkoxybutadienes with (chloromethylene)dimethylammonium chloride, obtained from dimethylformamide and carbonyl chloride (the Wilsmeier–Hagg reaction), Arnold[74] observed the formation of derivatives of glutaconaldehyde, which are cyclised in the reaction mixture under the action of ammonium salts into compounds of the pyridine series. It is interesting to note that such compounds are also formed by the acetals of crotonaldehyde and even by 1,1,3-trialkoxybutanes under the action of a formylating agent. This fact can evidently be explained only by the reaction of crotonaldehyde and

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1,1,3-trialkoxybutane acetals with the strongly electrophilic formylating agent producing intermediate 1-alkoxydienes, which also undergo formylation[74]:

$$CH_2=CH-CH=CHOR \xrightarrow{[(CH_3)_2N=CHCl]^+Cl^-} \rightarrow [(CH_3)_2N=CHCH=CHCH=CHOR]^+Cl^- \xrightarrow{OH^-} \rightarrow (CH_3)_2NCH=CH-CH=CH-CHO \xrightarrow{NH_4Cl}$$



Normant and Martin[24] made a detailed study of the formylation of some substituted 1-alkoxydienes with the aid of formylating agent from dimethylformamide and phosphoryl(V) chloride. This reaction gave a series of substituted unsaturated aminoaldehydes (LXI):

$$RCH=CR^1-CR^2=CHOC_2H_5 + [(CH_3)_2N=CHCl]^+[OPOCl_2] \rightarrow \rightarrow [(CH_3)_2NCHCl-CHR-CR^1=CR^2-CHOC_2H_5][OPOCl_2]^- \xrightarrow{-HCl} \rightarrow [(CH_3)_2NCH=CR-CR^1=CR^2-\overset{+}{C}HOC_2H_5 \longleftrightarrow (CH_3)_2\overset{+}{N}=CH-CR= =CR^1-CR^2=CHOC_2H_5][OPOCl_2]^- \xrightarrow{OH^-} (CH_3)_2N-CH=CR-CR^1=CR^2-CHO, \quad (LXI)$$

where R, R^1, R^2 = H or CH_3.

Normant and Martin[24] note certain features in the formylation of substituted 1-alkoxydienes. Thus with 1-ethoxy-3-methylbuta-1,3-diene the corresponding amino-aldehyde

$$(CH_3)_2N-CH=CH-CCH_3=CHCHO$$

could not be obtained. This is explained by the steric hindrance to electrophilic attack of the formylating agent by the terminal $CH_2=CCH_3$-group of the diene.

In the reaction of a formylating agent with 1-ethoxypenta-1,3-diene instead of the expected amino-aldehyde

$$(CH_3)_2NCH=CCH_3-CH=CHCHO \quad (LXII)$$

the amino-aldehyde

$$(CH_3)_2NCH=CHCH=CCH_3-CHO \quad (LXIII)$$

the structure of which was proved by the NMR method, was obtained. Normant and Martin[24] think that in the action of the formylating agent on 1-ethoxypenta-1,3-diene a carbonium ion normal for this diene salt is formed:

$$[(CH_3)_2N-CH=CCH_3-CH=\overset{+}{C}HOC_2H_5 \longleftrightarrow (CH_3)_2\overset{+}{N}=CH-CCH_3=CH-CH=CHOC_2H_5]$$

In the decomposition of this salt in alkaline medium initially the aminoaldehyde (LXII) is formed and also the dialdehyde

$$CHO-CCH_3=CHCH_2CHO \quad (LXIV)$$

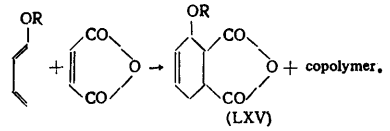
and dimethylamine (as a result of the hydrolysis of the excess of formylating agent). The dimethylamine liberated immediately reacts with the amino-aldehyde (LXII) and dialdehyde (LXIV) to form the isomeric cation

$$[(CH_3)_2NCH=CCH_3-CH=CHCH=\overset{+}{N}(CH_3)_2],$$

hydrolysis of which gives the more stable (LXIII).

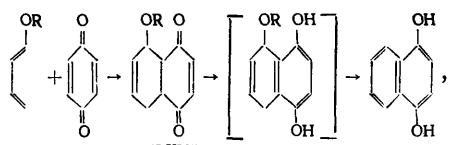
9. Diene Synthesis

The diene condensation of 1-alkoxybutadienes with maleic anhydride has been frequently studied[5,11,15,19,20,32,75,76]. Most authors[5,11,32,75] report that this reaction takes place very vigorously and leads to the formation of a normal addition product—the anhydride of 2-alkoxy-2,5,6-tetrahydrophthalic acid (LXV). Furthermore, the reaction is accompanied by the copolymerisation of 1-alkoxydiene with maleic anhydride:



(LXV)

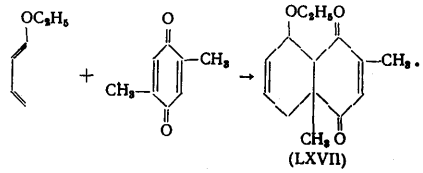
The reaction of 1-alkoxybutadienes with various quinones has been studied best. In the reaction of 1-methoxy- and 1-ethoxy-butadiene with *p*-benzoquinone addition products (LXVI) are formed, which lose alcohol under the influence of acetic acid and hydrogen bromide and are converted into 1,4-dihydroxynaphthalene[77]:



(LXVI)

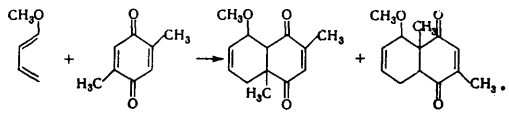
where R = CH_3, C_2H_5.

The reaction of 1-ethoxybutadiene with xyloquinone[78] gave only one isomer of the addition product, which was ascribed structure (LXVII) without proof:



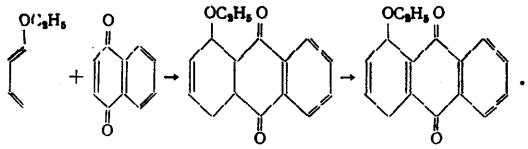
(LXVII)

The condensation of 1-methoxybutadiene with the same dienophile leads to a mixture of two structural isomers, the ratio of the amounts of *"ortho"* (LVIII) and *"meta"* (LXIX) isomers being 10 : 1:



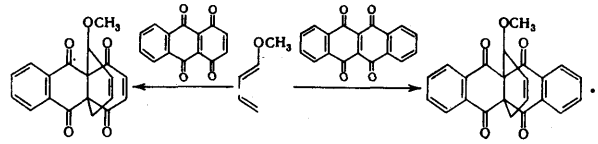
(LXIX) (LXVIII)

1-Ethoxybutadiene reacts readily with 1,4-naphthaquinone to form compound (LXX) which is readily oxidised by atmospheric oxygen to a dihydroanthraquinone derivative (LXXI)[11]:



(LXX) (LXXI)

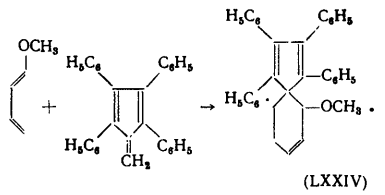
The condensation of 1-methoxybutadiene with quinizarin-quinone gives compound (LXXII) and that with tetracene-quinone gives compound (LXXIII)[79]:



(LXXII) (LXXIII)

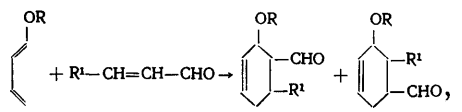
The condensation of 1-methoxybutadiene with tetraphenylfulvene gives an addition product (LXXIV) and in

condensation with tetraphenylpentadiene a substance whose structure has still not been explained is produced[80]:



(LXXIV)

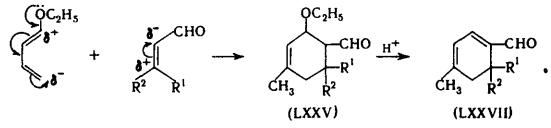
The diene condensation of 1-alkoxydienes with unsymmetrical dienophiles has been studied in a series of papers. Wichterle[1] was the first to condense unsaturated 1-alkoxybutadienes with acrylaldehyde and crotonaldehyde. He suggested that the addition products obtained contain both of the theoretically possible isomers:



where R^1 = H or CH_3. However, the structure of the addition products obtained was not proved.

The condensation of 1-cyclohexyloxybutadiene with crotonaldehyde was effected recently[5]. The authors, without giving any proof, consider that the addition product obtained is 3-cyclohexyloxy-2-methyl-1,2,3,6-tetrahydrobenzaldehyde (a *"meta"* adduct).

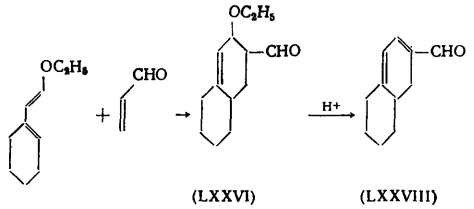
A special study[76] of the structural selectivity of the diene synthesis of 1-alkoxydienes with $\alpha\beta$-unsaturated aldehydes, revealed that the condensation of 1-ethoxy-3-methylbutadiene with acrylaldehyde, crotonaldehyde, and β-methylcrotonaldehyde leads to the formation exclusively of *"ortho"* addition products (LXXV) in accordance with the polarisation of the diene and dienophile:



(LXXV) (LXXVII)

The structure of the products (LXXV) was established chemically and by ultraviolet spectroscopy.

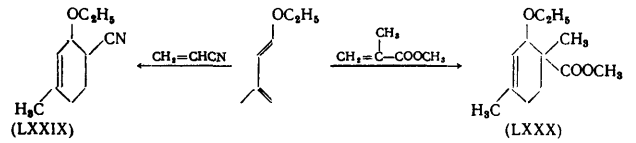
There is also structural selectivity in the reaction between 1-(β-ethoxyvinyl)cyclohexene and acrylaldehyde[76] with the formation of compound (LXXVI):



(LXXVI) (LXXVIII)

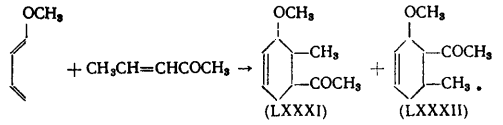
These reactions make accessible the cyclodialkenic aldehydes (LXXVII) and (LXXVIII) which are obtained by other methods in a much more complex manner.

1-Ethoxy-3-methylbutadiene readily undergoes a diene synthesis with acrylonitrile and methyl methacrylate to form 2-ethoxy-1,2,5,6-tetrahydro-4-methylbenzonitrile (LXXIX) and methyl 2-ethoxy-1,4-dimethylcyclohexene-3-carboxylate (LXXX). The reaction here is also structurally directed[76]:



(LXXIX) (LXXX)

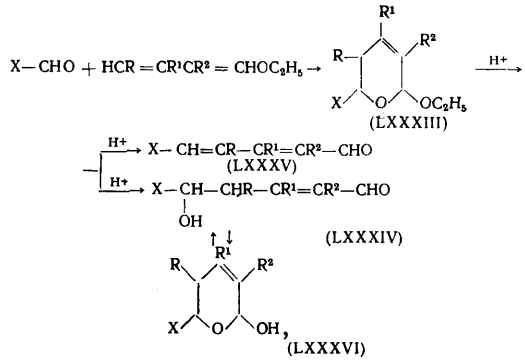
However, the condensation of methoxybutadiene with methyl propenyl ketone leads to a mixture of the two possible isomers (LXXXI) and (LXXXII)[81]:



(LXXXI) (LXXXII)

These isomers were separated by fractional distillation or (less successfully) chemically on the basis of the difference in activity of the carbonyl groups in the compounds (LXXXI) and (LXXXII) in the production of some of their derivatives.

The condensation of the 1-alkoxydienes with heterodienophiles has still been little studied. It was shown that 1-alkoxydienes are capable of undergoing a diene synthesis with paraform[82,83] and with aldehydes having electron-acceptor groups in the α-position—chloral and esters of glyoxylic acid[83]. In every instance the reaction leads to substituted 2-alkoxy-Δ^3-dihydropyrans (LXXXIII):

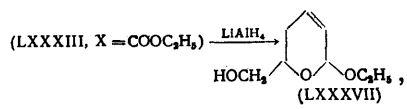


(LXXXIII) (LXXXV) (LXXXIV) (LXXXVI)

where X = H, $CCl_3COOC_2H_5$; R, R^1, R^2 = H, CH_3.

The hydrolysis of the dihydropyrans (LXXXIII) in acid medium allows either $\alpha\beta$-unsaturated δ-hydroxyaldehydes (LXXXIV) or ω-functionally substituted polyene aldehydes (LXXXV) to be obtained, depending on the reaction conditions. The compounds (LXXXIV) are in tautomeric equilibrium with their cyclic forms (LXXXVI).

6-Carboethoxy-2-ethoxy-Δ^3-dihydropyran (LXXXIII; X = $COOC_2H_5$) is readily reduced by lithium tetrahydroaluminate to give 2-ethoxy-6-hydroxymethyl-Δ^3-dihydropyran (LXXXVII) which is of interest as a starting material for the production of desoxysugars[83]:

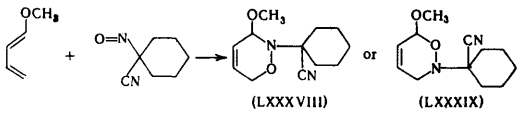


(LXXXVII)

where R^1 = R^2 = R^3 = H.

Finally, the condensation of 1-methoxybutadiene with 1-nitrosocyclohexanecarbonitrile has been described[84].

An addition product of structure (LXXXVIII) or (LXXXIX) is obtained in good yield:



(LXXXVIII) (LXXXIX)

10. Polymerisation of 1-Alkoxydienes

Due to the presence of an alkoxy-group, 1-alkoxydienes are rather strongly polarised and therefore tend mainly to ionic polymerisation. According to a patent [85] the polymerisation of 1-methoxybutadiene can be satisfactorily carried out in a reactor packed with kaolin. Clay, kaolin, hydrosilicates, etc. are used as catalysts, either pure or carried on silica gel or activated carbon. The solvents employed are petroleum ether, benzene, CCl_4, $CHCl_3$, etc. Liquid, viscous, and solid polymers were obtained in this way. Other authors [86] polymerised 1-methoxybutadiene using Ziegler catalysts: a polymer of crystalline structure was obtained, the infrared spectrum of which showed that it has a completely *trans*-structure.

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