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THE REACTIVITY OF ACETALS AND IONIC TELOMERISATION

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1. INTRODUCTION

Acetals are extremely reactive compounds, and have found increasing use during recent years as starting materials in various syntheses. Among the many methods for preparing acetals, an important current technique is their formation from unsaturated ethers based on acetylene and diacetylene. Thus acetals are obtained by the addition of alcohols to unsaturated ethers[1-13]:

$$CH{\equiv}CH \xrightarrow{ROH} CH_2{=}CH{-}OR \xrightarrow{ROH} CH_3{-}CH(OR)_2,$$

$$CH{\equiv}C{-}C{\equiv}CH \xrightarrow{ROH} CH{\equiv}C{-}CH{=}CH{-}OR \xrightarrow{ROH} CH_3{-}C{\equiv}C{-}CH(OR)_2,$$

or by the addition of orthoformic esters[14-16]:

$$CH_2{=}CH{-}OR + CH(OR)_3 \rightarrow (RO)_2CH{-}CH_2{-}CH(OR)_2,$$

$$CH{\equiv}C{-}C{\equiv}CH \rightarrow BrMg{-}C{\equiv}C{-}C{\equiv}C{-}MgBr \xrightarrow{CH(OR)_3} (RO)_2CH{-}C{\equiv}C{-}C{\equiv}C{-}CH(OR)_2,$$

$$CH{\equiv}C{-}CH{=}CH{-}OR \rightarrow BrMg{-}C{\equiv}C{-}CH{=}CH{-}OR \xrightarrow{CH(OR)_3} \rightarrow (RO)_2CH{-}C{\equiv}C{-}CH{=}CH{-}OR$$

$$CH{\equiv}C{-}CH{=}CH{-}SR \rightarrow BrMg{-}C{\equiv}C{-}CH{=}CH{-}SR \xrightarrow{CH(OR)_3} \rightarrow (RO)_2CH{-}C{\equiv}C{-}CH{=}CH{-}SR.$$

In this way various acetals, alkoxyacetals, and diacetals, containing alkoxy-, alkylthio-, or arylthio-groups, and perhaps also double and triple bonds in the carbon skeleton, can be synthesised from vinyl ethers, ethynylvinyl ethers, and sulphides based on acetylene and diacetylene, and also from diacetylene itself.

A great deal of work has recently appeared in the chemical literature on the synthesis of various polyene and polyenyne compounds (for example isoprenoids). Acetals are often employed as starting materials in these syntheses. Furthermore, acetals are able to undergo ionic telomerisation with vinyl ethers and sulphides (this constitutes a new trend in the use of these compounds). Since new unsaturated compounds containing an acetal group are beginning to be employed in these interesting syntheses, it seemed to us profitable to summarise the disconnected experimental results available on this question.

The present review will deal mainly with new or little known reactions of acetals, which are from our point of view the most promising and are of interest for the chemistry of acetals in general.

Acetals can react differently, depending on their structure and the reaction conditions, the carbonyl group, substituents, or multiple bonds being involved in the reaction. Acetals are characterised by many chemical reactions, including hydrolysis, symmetrisation, hydrogenation, condensation, etc., which have been described by various workers[1,10-13,18-28].

2. NON-CATALYTIC AND IONIC REACTIONS OF ACETALS

Non-catalytic reactions of acetals are readily explained in terms of hydrogen bonding[29], the role of which in the formation of acetals has been discussed by Shostakovskii[1,12]. This hypothesis was later supported by optical measurements[30]. A hydrogen bond formed between the oxygen atom of the vinyl ether and the alcoholic hydrogen produces an intermediate compound[30], which can dissociate reversibly under certain temperature conditions, yielding molecules of vinyl ethers and of alcohols containing different radicals. Interaction between vinyl ether and alcohol molecules containing identical radicals results in the formation of symmetrical acetals. Thus the reaction mixture contains all possible acetals.

$$CH_2{=}CH{-}OR + R'OH \rightleftarrows CH_2{=}CH{-}OR \rightleftarrows CH_3{-}CH\begin{matrix}OR\\OR'\end{matrix},$$
$$\vdots$$
$$H{-}O{-}R'$$

$$CH_3{-}CH\begin{matrix}OR\\OR'\end{matrix} \rightleftarrows CH_2{=}CH{-}OR' \rightleftarrows CH_2{=}CH{-}OR' + ROH.$$
$$\vdots$$
$$H{-}O{-}R$$

This concept explains the mechanism of such reactions as the non-catalytic formation of acetals from vinyl ethers and alcohols on heating, and the trans-etherification of mixed into symmetrical acetals on distillation. The thermal decomposition of acetals into vinyl ethers and alcohols, which is often used for preparative purposes[1], must be regarded as a reaction of this type.

Similarly, pyrolysis of an acetaldehyde monothioacetal involves its decomposition with the elimination of an

alcohol molecule and formation of 2-butoxyethyl vinyl sulphide[31]:

$$CH_3-CH\begin{matrix}OC_4H_9\\SCH_2CH_2OC_4H_9\end{matrix} \xrightarrow{\Delta} CH_2=CH-SCH_2CH_2OC_4H_9 + C_4H_9OH.$$

It is interesting that in this case it is the alkoxy- and not the alkylthio-radical of the acetal which is eliminated, indicating the greater lability of the former. Most reactions of acetals, however, take place in the presence of catalysts and by an ionic mechanism.

Among ionic reactions involving exchange of alkoxy--groups in acetals, those with aldehydes and ketones have been described[32]. A redistribution of alkoxy-groups takes place, the reaction being reversible. The reactions of acetals of acetaldehyde with butyraldehyde, benzaldehyde, furfuraldehyde, cyclohexanone, and acetophenone, for example, can be represented by the scheme

$$R-CHO + CH_3-CH(OC_4H_9)_2 \rightleftarrows R-CH(OC_4H_9)_2 + CH_3CHO,$$
$$(R)_2CO + CH_3-CH(OC_4H_9)_2 \rightleftarrows (R)_2C(OC_4H_9)_2 + CH_3CHO.$$

Reactions of acetals of another type are those in which the hydrogen atoms of the aldehyde take part. In an investigation of hydrogen exchange between the diphenyl acetal of acetaldehyde and liquid deuterated ammonia (ND_3) with KND_2 as catalyst[33] it was found that one of the five hydrogen atoms exchanged for deuterium comes from the aldehyde part of the acetal, and in our opinion from the methine group, since hydrolysis of this acetal yielded acetaldehyde containing a deuterium atom attached directly to the carbonyl group[34]:

$$CH_3-CD(OC_6H_3D_2)_2 \rightarrow CH_3-CDO.$$

Hence under certain conditions the methine hydrogen in the diphenyl acetal of acetaldehyde is reactive in solution in liquid deuterated ammonia, which possesses well defined basic properties. It is interesting that exchange does not take place in the dibutyl acetal under these conditions.

When the dibutyl acetal reacts with phenyl vinyl ether in the presence of the boron trifluoride–ether complex, the reaction products include the dibutyl acetal of 3-phenoxybutyraldehyde. This fact does not exclude the possibility that the reaction takes place by exchange of a 2-hydrogen atom of the acetal[34]:

$$\overset{2}{CH_3}-\overset{1}{CH}(OC_4H_9)_2 + CH_2=CH-OC_6H_5 \rightarrow CH_3-\overset{3}{CH}(OC_6H_5)-\overset{2}{CH_2}-\overset{1}{CH}(OC_4H_9)_2$$
$$CH_3-CH(OC_6H_5)-CH_2-CHO.$$

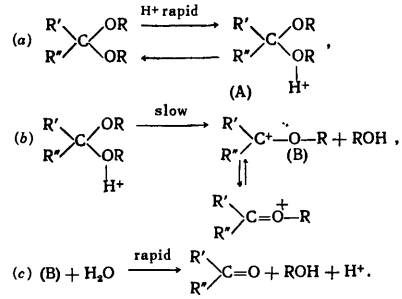
Hydrolysis of acetals is among the most typical ionic reactions of these compounds, on which a great amount of work has been done. This reaction takes place in acid medium and yields the aldehyde and the alcohol[1]:

$$R-CH(OR')_2 + 2H_2O \rightarrow RCHO + 2R'OH.$$

Various acidic reagents are employed for the hydrolysis, depending on the structure of the acetals: oxalic[35], tartaric[36,37] citric[38], benzenesulphonic[39], perchloric[40], trifluoroacetic[41], and acetic[42,43] acids, boron trifluoride[44], and also ion-exchange resins[45].

Investigation of the influence of various conditions and factors on the rate of hydrolysis of acetals has shown that those containing alkyl radicals are readily hydrolysed in the cold, but the rate falls with increase in their molecular weight. This reaction is greatly influenced by polarity, conjugation[47], and steric effects[46]. Kreevoy and Taft[47] studied the rate of hydrolysis of various acetals and ketals in aqueous dioxane at 25°, and found that with acetals of $\alpha\beta$-unsaturated aldehydes conjugation is the main factor in preventing hydrolysis. This is confirmed with acetals of aldehydes containing an enyne grouping, obtained from diacetylene. These acetals and their alkoxy--derivatives are not hydrolysed under normal conditions.

The mechanism of the hydrolysis of acetals in acid medium has now been quite fully investigated, and can be represented by the scheme[48]



In the first stage (*a*) an ether oxygen atom undergoes cationic attack, resulting in the formation of an "oxonium cation" (A), which decomposes slowly into a cation (B) and an alcohol. Stage (*b*) determines the rate of hydrolysis. In the following stage (*c*) the cation (B) is converted *via* the hemiacetal into the final carbonyl compound.

The thermal decomposition of acetals to form a vinyl ether and an alcohol often takes place considerably more readily and more rapidly in the presence of a catalyst. Many investigators[49–53] have studied this reaction with the aim of developing the most effective method for synthesising various vinyl ethers and alkoxybutadienes. The catalysts used for these purposes were sulphates and phosphates of sodium, magnesium, and aluminium, activated charcoal, clay, $BaO.SiO_2$, etc.

Elimination of an alcohol from acetals may take place both in the vapour and in the liquid phase. Makin and Kruptsov[53] worked out a method for synthesising alkoxybutadienes by vapour-phase and liquid-phase methods in the presence of salts of phosphoric acid:

$$CH_2(OR)-CH-CH(OR)_2 \xrightarrow{-2ROH} CH=C-C=CH-OR.$$
(R′, R″, R‴)

A new and interesting reaction of acetals is their dimerisation and trimerisation, studied by Yufit and Kucherov[44,54–56] with acetals of saturated and unsaturated aldehydes. Dimerisation of the former takes place in the presence of boron trifluoride or zinc chloride and involves the elimination of an alcohol molecule. Thus the diethyl acetal of acetaldehyde dimerises into 1,1,3-triethoxybutane, which was isolated in up to 50% yield:

$$2CH_3-CH(OC_2H_5)_2 \rightarrow CH_3-CH(OC_2H_5)-CH_2-CH(OC_2H_5)_2 + C_2H_5OH.$$

In the case of the interaction of the acetals of two different aldehydes dimerisation also involves a 2-hydrogen atom of one of the acetals, resembling in this

respect the scheme for the reaction of acetals with vinyl ethers:

$$R{-}CH(OC_2H_5)_2+R{-}CH_2{-}CH(OC_2H_5)_2 \rightarrow R{-}CH(OC_2H_5){-}CH(R){-}CH(OC_2H_5)_2+C_2H_5OH.$$

The dimerisation products readily split off alcohol molecules to form unsaturated compounds.

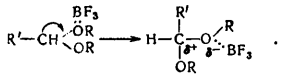
In the opinion of these workers[44], the dimerisation and trimerisation of acetals of $\alpha\beta$-unsaturated aldehydes involves a double bond conjugated with the acetal group and sufficiently active to add on a second and a third molecule of the same acetal:

$$2R{-}CH{=}CH{-}CH(OR)_2 \rightarrow R{-}CH{=}CH{-}\underset{\displaystyle OR}{\underset{|}{CH}}{-}\overset{\displaystyle R{-}CH{-}OR}{\overset{|}{CH}}{-}CH(OR)_2.$$

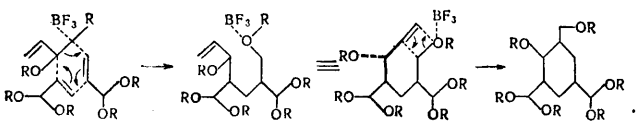
Thus the diethyl acetal of crotonaldehyde readily dimerises under the influence of boron trifluoride, but that of acrolein reacts with greater difficulty, the main product being the trimer.

Yufit and Kucherov[54-56] found that their results for the dimerisation of acetals of $\alpha\beta$-unsaturated aldehydes could not be explained by a mechanism based on the intermediate formation of a carbonium ion. In the low-temperature dimerisation of acrolein acetal under the influence of BF_3 they detected the formation of a cyclic trimer in addition to the normal dimer and a linear trimer. They consider that the classical ionic views of the mechanism of addition and substitution reactions of acetals are not always entirely satisfactory, and that such reactions can be explained in a different way, by cyclic electron transfer[57,58].

Addition of BF_3 to an oxygen atom in the acetal group *via* a lone pair of electrons destroys the electronic symmetry of the group, producing strong polarisation of the C–O bond. This polarisation is intensified by the presence of a double bond in the $\alpha\beta$-position, and can easily be involved, through cyclic electron transfer, in addition and substitution reactions:



The formation of a cyclic trimer in the reaction is explained by the formation of a quasiaromatic complex containing six electrons in the field of six nuclei, this being subsequently stabilised to yield the trimer:



3. EXCHANGE OF ALKOXY-GROUPS IN ACETALS

The most widely known reactions of acetals, which enable them to be used as starting materials in various syntheses, are those involving the exchange of alkoxy-groups. First of all there is the well known Chichibabin reaction[59], which consists in the exchange of an alkoxy-group for the hydrocarbon radical of an organomagnesium complex, to yield the corresponding ether:

$$CH_3{-}CH(OR)_2+BrMgR' \rightarrow CH_3{-}CHR'{-}OR.$$

This reaction has now been extended to many acetals[60,61], and several peculiarities have been found depending on the structure of the radical. In mixed acetals, for example, the heavier alkoxyl exchanges more readily, while in symmetrical acetals the capacity of the alkoxy-groups for exchange decreases in the following sequence:

$$OC_6H_5>OAlK>OCH_2C_6H_5.$$

If the alkoxy-groups of the acetal contain halogen, this is exchanged for the radical of an organomagnesium complex on reaction with the latter. Thus a bis-2-chloroethyl acetal with benzylmagnesium chloride yielded the bis-3-phenylpropyl acetal[62]:

$$CH_3{-}CH(OCH_2CH_2Cl)_2+2C_6H_5CH_2MgCl \rightarrow CH_3{-}CH(OCH_2CH_2CH_2C_6H_5)_2+2MgCl_2.$$

When acetals react with alcohols containing radicals other than those in the acetal, interchange of the radicals takes place[63]:

$$R{-}CH(OR')_2+R''OH \rightleftarrows RCH\begin{matrix}OR'\\OR''\end{matrix} \longrightarrow R{-}CH(OR'')_2.$$

This reaction forms the basis of a well-known method for synthesising various mixed and symmetrical acetals[64]. Mkhitaryan[65] carried out this reaction with pentaerythritol, which under the influence of catalytic amounts of *p*-toluenesulphonic acid reacts with acetals of various aldehydes to form cyclic acetals:

$$2R{-}CH(OR')_2+\begin{matrix}HOCH_2\\HOCH_2\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_2OH\\CH_2OH\end{matrix} \longrightarrow R{-}CH\begin{matrix}OCH_2\\OCH_2\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_2O\\CH_2O\end{matrix}\!\!>\!CH{-}R+4R'OH.$$

An interesting reaction is that of acetals with thionyl chloride and phosphorus pentachloride: the alkoxy-group of the acetal is exchanged for halogen, yielding chlorinated alkoxyalkanes. Thus Skoldinov and Protopopova[66] were the first to obtain 1,3-dialkoxy-1,3-dichloropropanes from acetals of malonaldehyde. These are very reactive compounds readily forming a series of derivatives:

$$(RO)_2CH{-}CH_2{-}CH(OR)_2 \xrightarrow{SOCl_2;\ PCl_5} RO{-}CHCl{-}CH_2{-}CHCl{-}OR.$$

We have used this reaction to synthesise alkyl and aryl 1-chloroethyl ethers from the corresponding acetals of acetaldehyde:

$$CH_3{-}CH(OR)_2 \xrightarrow{SOCl_2} CH_3{-}CHCl{-}OR.$$

This reaction goes smoothly when equimolar quantities, for example of the dibutyl acetal of acetaldehyde and of thionyl chloride, are mixed in the presence of catalytic amounts of pyridine at 70°–80°, and results in the formation of the butyl 1-chloroethyl ether, isolated in 72% of theoretical yield.

With alkoxyacetals of the type $RO{\cdot}CH{:}CH{\cdot}C{\vdots}C{\cdot}CH(OR)_2$, based on diacetylene, however, it proved impossible to carry out this reaction under the above conditions. It is probable that here, as in the hydrolysis of these compounds, conjugation in the carbon chain greatly influences the mobility of the alkoxy-groups.

Arnold and Šorm[67-69] have described the formylation of acetals by treating them with dimethylformamide and carbonyl chloride:

$$R{-}CH(OC_2H_5)_2 \xrightarrow[COCl_2]{(CH_3)_2NCHO} [(CH_3)_2N{-}CH{=}\underset{\displaystyle R}{\underset{|}{C}}{-}CH{=}N(CH_3)_2]^+Cl^- \rightarrow$$

$$\rightarrow (CH_3)_2N{-}CH{=}\underset{\displaystyle R}{\underset{|}{C}}{-}CHO \longrightarrow CHO{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}CHO.$$

They carried out this reaction also with vinyl ethers, 1-chloroalkyl ethers, and ketals[68], and used it to synthesise various aliphatic alkylidenedialdehydes. If acetals

of crotonaldehyde are subjected to formylation under these conditions, it is possible to synthesise nicotinic aldehyde[69]:

$$CH_3-CH=CH-CH(OC_2H_5)_2 \xrightarrow[(CH_3)_2NCHO]{-C_2H_5OH} [CH_3=CH-CH=CH-OC_2H_5] \rightarrow$$

$$\rightarrow (CH_3)_2N-CH=CH-CH=CH-CHO.$$

In this case, as also when the acetal of 3-ethoxybutyraldehyde was used as starting material, the reaction involved the intermediate formation of 1-ethoxybuta-1,3-diene.

In this type of exchange reactions can be included the reaction of acetals with alkane- and arene-thiols, which we have recently studied[8,15,70] and which gives a good yield of mercaptals:

$$R-CH(OR')_2+2AlkSH \rightarrow R-CH(SAlk)_2+2R'OH,$$

where $R=CH_3$, $CH_3-C\equiv C$, $CH_3CH(OC_4H_9)-CH_2$; $R'=C_2H_5$, C_4H_9;

$$RX-CH=CH-C\equiv C-CH(OR')_2+R'SH \rightarrow (R'S)_2-CH-CH_2-C\equiv C-CH(SR')_2,$$

where $RX=C_2H_5S$, C_4H_9O; $R'=C_2H_5$.

This reaction can be extended to ketals and orthoformic esters, and a method for synthesising various mercaptals, mercaptols, and thioorthoformic esters was worked out on its basis[71]:

$$\begin{matrix}R\\R'\end{matrix}\!\!>\!C(OR'')_2+AlkSH \longrightarrow \begin{matrix}R\\R'\end{matrix}\!\!>\!C(SAlk)_2+2R''OH,$$

$$CH(OR)_3+AlkSH \longrightarrow CH(SAlk)_3+3ROH.$$

Reaction takes place on slight warming in the absence of catalysts. However, it proved difficult to prepare dimercaptals containing aromatic radicals by this method, and in both cases (I) and (II) the reaction stopped at the formation of the mixed mercaptals, probably owing to the low reactivity of the alkoxy-group in the mixed mercaptal under these conditions:

$$CH_3-CH(OAr)_2 \xrightarrow{AlkSH} CH_3-CH\begin{matrix}OAr\\SAlk\end{matrix}, \quad (I)$$

$$CH_3-CH(OArk)_2 \xrightarrow{ArSH} CH_3-CH\begin{matrix}OAlk\\SAr\end{matrix}. \quad (II)$$

4. REACTIONS OF ACETALS WITH VINYL ETHERS AND IONIC TELOMERISATION

This type of exchange reaction can be taken to include the interesting and promising reactions of acetals with various vinyl compounds. Among such reactions are those of acetals with vinyl ethers[34,72-77], with 1- and 2-substituted vinyl ethers[78-80], 1-alkoxybut-1-en-3-ynes[81], 1-ethoxyalka-1,3-dienes[22], and vinyl sulphides[23]. The reaction with vinyl ethers was carried out not only with acetals of aliphatic aldehydes but also with those of aromatic aldehydes[24-26,73], dialdehydes[27,78], alkoxyaldehydes, and alkyl(aryl)thio-aldehydes[23] containing a pentenyne carbon chain.

Reactions of acetals with vinyl ethers have become more and more widespread during recent years as a result of the search for new ways of building up carbon chains in the molecules of various unsaturated compounds. For example, reactions of acetals with vinyl ethers are widely employed in the synthesis of isoprenoid chains[73]. Isler and others[75,76] used this method to synthesise β-carotene from β-ionone as starting material. These papers have been discussed in detail in Yanovskaya's reviews[28,82] of the various methods for building up carbon chains, and therefore we shall consider only the later work which is of interest from the point of view of ionic telomerisation.

A thorough study of the condensation of acetals with vinyl ethers was first made by Hoaglin and Hirsh[72], who suggested two possible ways in which this reaction could occur:

$$CH_3-CH(OR)_2+CH_2=CH-OR' \begin{cases} \rightarrow CH_3-CH(OR)-CH_2-CH\begin{matrix}OR\\OR'\end{matrix} & (I)\\ \rightarrow CH_3-CH(OR')-CH_2-CH(OR)_2. & (II)\end{cases}$$

With ethyl vinyl and butenyl ethyl ethers as examples, they showed that this reaction takes place according to pathway (I).

Later work with acetals and vinyl ethers containing alkyl radicals confirmed the correctness of this scheme. If, however, vinyl ethers containing radicals differing in structure from those in the acetals, for example aryl radicals, are subjected to this reaction, a mixture of substances is obtained, among which are found compounds indicating that the reaction may occur according to pathway (II), *i.e.* by splitting off a 2-hydrogen atom of the acetal. Thus in the reaction of dibutyl acetal with phenyl vinyl ether in the presence of BF_3 we were able[34] to isolate from the reaction mixture 1,1-dibutoxy-3-phenoxybutane, which gave on hydrolysis 3-phenoxybutyraldehyde.

Vinyl ethers interact differently with acetals containing unlike radicals, depending on the reactivity of the ethers and the nature of the aldehydes forming the acetals. Moreover, mixtures are formed in this case also, the separation of which is very difficult, and is aggravated by symmetrisation of the mixed acetals.

The addition of vinyl ethers to acetals is an electrophilic ionic reaction involving the intermediate formation of a complex of the acetal with BF_3, $ZnCl_2$,[72] or $FeCl_3$, decomposition of which liberates a carbonium ion $CH_3\cdot\overset{+}{C}H\cdot OR$ and an alkoxy-group as an anion, which add on to the double bond of the vinyl ether[72].

Study of the conditions and products of reactions between acetals and vinyl ethers showed that reaction does not stop at the addition of one molecule of the ether to the original acetal, the resulting alkoxyacetal adding on the next molecule of vinyl ether, and so on, until various polyalkoxy-alkanes, -alkenes, or -alkenynes have been formed, so that this reaction can be regarded as a telomerisation taking place by an ionic mechanism. The authors of these papers[23,34,72,74] were able, by carrying out this reaction in the presence of various catalysts (BF_3, $ZnCl_2$, $FeCl_3$), to isolate telomeric products of the general formula

$$CH_3-CH(OR)-[-CH_2-CH(OR)-]_n-CH_2-CH(OR)_2,$$

the proportions of which depend on those of the original ether and acetal, and also on the rates of the subsequent stages in the reaction, *i.e.* on the addition of a vinyl ether molecule to the polymeric products.

Telomerisation reactions are now being studied on a broad front, but this applies mainly to radical telomerisation, investigated with various unsaturated hydrocarbons[83,84], sulphur-containing compounds[85], some vinyl esters[86], and ethers with CCl_4,[87-89] and also vinyl ethers in the presence of various radical initiators[90-93].

Investigations of ionic telomerisation have been concerned also mainly with diene hydrocarbons in the presence of $SnCl_4$[94,95].

Little has been published on the ionic telomerisation of oxygen-containing compounds.

Heslinga[96] investigated the ionic telomerisation of styrene with formaldehyde in acetic acid, the reaction being catalysed by concentrated sulphuric acid at room temperature.

Reaction between formaldehyde and styrene under the influence of sulphuric acid was first achieved by Prins[97]. He isolated an equimolar addition product, and assumed it was 2-phenyl-1,3-propanediol, which later workers found to be erroneous. Subsequently it was found[98] that this reaction is telomeric in character, and a fraction containing dimeric acetates of aromatic $\alpha\omega$-glycols having the structure

$$HO-[-CH(C_6H_5)-CH_2-]_n-CH_2OH\ ,$$

was isolated. The same paper describes the ionic telomerisation of styrene with acetic acid and with acetonitrile, esters containing 1–3 styrene molecules, $H[CH_2\cdot CH(C_6H_5)]_n\cdot O\cdot CO\cdot CH_3$, being isolated in the first case, and acyl derivatives of primary amines, identified as $H[CH_2\cdot CH(C_6H_5)]_n\cdot NH_2$, in the second case.

Heslinga[96] studied the effect of varying the conditions of the Prins reaction on the composition of the final products, investigated quantitative aspects of the reaction, and isolated telomers of the general formula

$$CH_3CO-[-CH(C_6H_5)-CH_2-]_n-CH_2OH.$$

He discusses in detail the mechanism of this reaction, and considers that it involves the intermediate formation of a carbonium ion, $C_6H_5\cdot\overset{+}{C}H\cdot CH_2\cdot CH_2OH$, by the interaction of protonated formaldehyde with styrene. This ion adds on a second, etc. styrene molecule, or else terminates chain growth by adding on an acetate ion:

$$CH_2{=}CH(C_6H_5) \xrightarrow{CH_2OH} \overset{+}{C}H(C_6H_5)-CH_2-CH_2OH \xrightarrow{nC_6H_5-CH=CH_2} -[-\overset{+}{C}H(C_6H_5)-CH_2-]_n-CH_2OH \xrightarrow{AcOH}$$

$$AcO-[-CH(C_6H_5)-CH_2-]_n-CH_2OH+H^+.$$

Apart from the above investigations we may mention here a Japanese patent[99] describing the preparation of vinyl polyalkoxyacetals from vinyl ethers in the presence of mixed catalysts, for example $(CH_3COO)_2Hg$ or HgO with BF_3 complexes. From methyl vinyl and ethyl vinyl ethers, they obtained a mixture of products of the general formula $CH_2{:}CH\cdot[CH_2\cdot CH(OR)]_n\cdot CH_2\cdot CH(OR)_2$, from which they isolated compounds having carbon chains up to C_8.

5. IONIC TELOMERISATION REACTIONS OF ALKOXY-ACETALS AND ALKYLTHIOACETALS WITH VINYL ETHERS AND SULPHIDES

Quite recently we have investigated the ionic telomerisation occurring when alkoxyacetals and alkylthioacetals react with vinyl ethers and sulphides in the presence of $ZnCl_2$.[23] In the case of the alkyl vinyl ethers the reaction can be represented by the scheme

$$(C_2H_5O)_2CH-C{\equiv}C-CH{=}CH-OR\ (SR) \xrightarrow{CH_2=CH-OC_2H_5} (C_2H_5O)_2CH-$$

$$-[-CH_2-CH(OC_2H_5)-]_n-C{\equiv}C-CH{=}CH-OR\ (SR).$$

This reaction leads to the formation of a mixture of telomeric products containing C_{15} and longer carbon chains.

In contrast to the reaction of vinyl ethers with acetals of acetaldehyde, the first molecule of the ether adds on more slowly than subsequent molecules, which is probably due to a decrease in activity of the alkoxy-groups in the initial acetal under the influence of the neighbouring triple bond. This may well explain the more ready formation of higher telomerisation products. In the interaction of ethyl vinyl ether with the butoxyacetal an addition product containing one molecule of the ether and a C_7 carbon chain was isolated, as well as a C_{15} product containing five molecules of the vinyl ether. Of the addition products of the vinyl ether to the ethylthio-acetal, those containing one and three molecules of the vinyl ether, with C_7 and C_{11} carbon chains respectively, were isolated.

The use of vinyl sulphides in this reaction represents the first example of the participation of these compounds in ionic telomerisation. Before the present investigation the addition of ethyl vinyl sulphide to the diethyl mercaptal of acetaldehyde in the presence of the ether complex of BF_3 had been described[100]. Under the reaction conditions employed, however, the reaction did not occur telomerically, but stopped at the equimolar addition of the starting materials, addition of a second molecule of the vinyl sulphide being effected by taking the equimolar addition product as starting material.

Reaction of vinyl sulphides with alkylthio-acetals containing a pentenyne grouping, which we have investigated[23], yields a mixture of telomeric products and occurs according to the scheme

$$RS-CH{=}CH-C{\equiv}C-CH(OR)_2 \xrightarrow{CH_2=CH-SR} RSCH{=}CHC{\equiv}C-CH(OR)CH_2CH\langle^{OR}_{SR} \longrightarrow RSCH{=}CHC{\equiv}CCH(OR)CH_2CH(SR)_2(OR)_2$$

$$RSCH{=}CHC{\equiv}C-CH(OR)CH_2CH\langle^{OR}_{SR} \xrightarrow{CH_2=CH-SR} RS-CH{=}CH-C{\equiv}C-CH(OR)-[-CH_2-CH(SR)]_n-CH_2-CH\langle^{OR}_{SR}$$

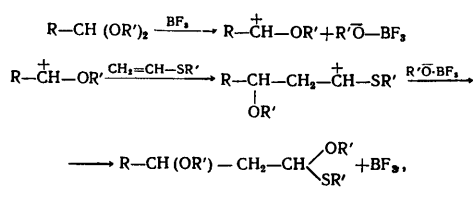
$$RS-CH{=}CH-C{\equiv}C-CH(OR)-[-CH_2-CH(SR)-]_n-CH_2-CH(SR)_2(OR)_2,$$

where $R = C_2H_5$ and $n = 1$ or 2.

Apart from extending the carbon skeleton of unsaturated acetals, this reaction makes it possible to introduce alkylthio-radicals into their molecules, yielding compounds containing sulphur (2 substituent groups).

In the early stages the mechanism of the successive addition of the vinyl sulphide to the unsaturated alkylthio--acetals is probably similar to that of the addition of vinyl ethers to acetals of acetaldehyde, and consists in the splitting off, under the influence of the catalyst, of an alkoxy-group of the acetal as an anion followed by addition of this anion and the resulting cation at the double bond of the vinyl sulphide. The mixed mercaptal which is thus formed reacts in a similar manner with the next vinyl sulphide molecule, and so on, the ion responsible for the subsequent process being the complex cation $RS\cdot CH{:}CH\cdot C{:}C\cdot CH(OR)\cdot[CH_2\cdot CH(SR)]_n\cdot CH_2\cdot\overset{+}{C}H\cdot SR$. The reaction can be terminated by symmetrisation of the

mixed mercaptals, as was proved by the quantitative "mercuric chloride" titration of the telomer end-groups:



where R = $C_2H_5 \cdot S \cdot CH{:}CH \cdot C{:}C -$.

These reactions enabled us to synthesise various polyalkoxy-acetals and polyalkylthio-acetals containing a C_{15} carbon chain, and also alkoxy-mercaptals having a C_{11} chain with a conjugated system of double and triple bonds.

The ionic telomerisation of oxygen- and sulphur--containing unsaturated compounds is a promising field in the chemistry of high polymers. Apart from their intrinsic value for synthetic purposes, the resulting products can serve as models for studying the structure of the end-groups of macromolecular compounds, in particular the polymers of vinyl ethers and sulphides. This is very important also in studying the ionic polymerisation and copolymerisation of many ethers[101-103], for example aryl vinyl ethers, when polymers of low molecular weight whose structure has not yet been adequately elucidated, are obtained.

This investigation of the chemical properties of various unsaturated alkoxy- and alkylthio-acetals, synthesised on the basis of diacetylene, has shown that these compounds are very reactive. Their interaction with vinyl ethers and sulphides under the influence of ionic catalysts results in telomerisation with the formation of various polyalkoxy (or alkylthio)-alkenynes, which are telomeric products having acetal or mercaptal end-groups.

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XYLAN

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1. INTRODUCTION

Xylan is the chief polysaccharide among the hemicelluloses of cereals and many other plant raw materials. Increasing attention has been paid during recent years to the investigation of its structure and properties, and the results obtained have considerably extended our knowledge of the hemicelluloses[1,2].