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Synthesis of Vinyl Ethers Containing Functional Groups and Heteroatoms

M.F.Shostakovskii, B.A.Trofimov, A.S.Atavin, and V.I.Lavrov

The paper gives a brief analysis of the chief methods for synthesising vinyl ethers containing functional groups and heteroatoms. Published information on the Favorskii-Shostakovskii reaction—the direct vinylation of hydroxylated compounds (alkoxyalkanols, glycols, polyhydric alcohols)—is surveyed, the mechanism of the reaction is discussed, and its application considered to the vinylation of nitrogen-containing alcohols (amino-alcohols and amino- and nitro-phenols), and to alkylthio-alcohols, silicon-containing alcohols, halogenated alcohols, and halogenated phenols. The elimination of hydrogen halides from halogenated ethers and the reaction of vinyl exchange are also reviewed. Methods are discussed based on the reactions of functional groups in substituted vinyl ethers (vinyloxyalkanols and halogenated and nitrogen-containing vinyl ethers), catalytic elimination in functional acetals, and the interaction of halogenated acetals with metals and of alkoxides of functional alcohols with vinyl halides. The fields of application of each of the above methods are assessed. A list of 302 references is included.

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I. INTRODUCTION

The increasing amount of research on $\alpha\beta$-unsaturated ethers containing reactive functional groups has long ago made it necessary to summarise and analyse in detail the available experimental information. A monograph[1], review papers[2-6], and numerous theses[7-21] from the Favorskii–Shostakovskii school have covered more or less fully only the vinyl ethers of alcohols containing no functional substituents. The present paper gives a brief analysis of the principal methods for the synthesis of functional vinyl ethers, and an attempt is made as far as possible to assess the field of application of each of them. Alkoxyethylenes containing substituents in the vinyl group, vinyl sulphides, and vinylamines are not discussed.

II. THE FAVORSKII–SHOSTAKOVSKII REACTION

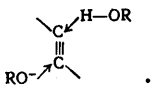
Direct vinylation, i.e. the addition of hydroxylated compounds to acetylene in the presence of basic catalysts (the Favorskii–Shostakovskii reaction[22,23]), is at present the most widely used method for preparing vinyl ethers. The simplicity of the synthesis, its completion in one stage, the availability of the starting material, and the almost quantitative yields of the required products make this a convenient method for industrial application. An obstacle to its wide introduction into industry is the need to use high pressures in individual cases: this, of course, increases the likelihood of explosion of the acetylene[24], but the danger is often greatly exaggerated[25].

The work of the Favorskii–Shostakovskii school[1,23,26-30] had already demonstrated by the end of the 1930s, independently of Reppe's work[31,32], the possibility of accomplishing industrial syntheses based on acetylene under pressure. In contrast to the patents of the IG. Farbenindustrie AG.[33-35], which envisaged dilution of the acetylene with an inert gas, a more intensive technology was developed in the USSR, under conditions of the inevitable dilution of the acetylene with the vapours of the starting material to be vinylated and the vinyl ethers formed, which are reliable stabilisers.

1. Mechanism of the Reaction

In spite of isolated attempts to make the problem a matter of controversy[36,37], the view has become accepted, strengthened by chemical kinetic data[38-40], that the process is a typical case of nucleophilic addition at the triple bond[41,42]. Vinylation has already been cited[43] as a classic example of nucleophilic addition to acetylenic systems. Nevertheless, examples exist[44,45] which do not fit well into such a scheme.

A detailed examination of the mechanism of vinylation has recently been made in a review[41] and in theses[18,21,46]. However, several aspects of the problem have been left untouched. Nucleophilic vinylation can be interpreted most acceptably as a concerted *trans*-addition:



This scheme[47] explains perfectly satisfactorily the main features of vinylation—(*a*) preferential formation of *cis*-adducts[38,41], (*b*) oriented addition to monosubstituted acetylenes, with formation of β-isomers when an acceptor substituent (phenyl[38,42,48], trifluoromethyl[49], diethoxymethyl[50]) is present at the triple bond, and formation of the α-isomer if acetylene containing a donor substituent is involved in the reaction[50], (*c*) the difficulty of reaction when donor substituents are present at the triple bond[51], and (*d*) increase in rate of reaction with increase in the nucleophilic character of the reagent[40,44,52]. In cyclic mechanisms *cis*-addition is assumed, although there has probably not yet been an example of the isolation of *trans*-adducts, which should be formed in this case.

Analysis of the literature in terms of simultaneous nucleophilic addition permits us to explain tentatively several known generalisations and discrepancies associated with vinylation which hitherto have not been entirely clear. Thus the presence of water sharply diminishes the rate of vinylation of aliphatic alcohols[1,4,26], whereas it definitely promotes the vinylation of phenols[40,44,52] and thiols[53,54]. In the absence of solvents or in non-polar media, phenols yield vinyl ethers under considerably more severe conditions than do aliphatic alcohols[37,46]. Yet in the vinylation of phenols in an alcoholic medium, under conditions close to those used for the vinylation of aliphatic alcohols, the corresponding aryl vinyl ethers are formed smoothly[55]. In all these cases a number of acid–base equilibria (alcohol, water, alkali, alkoxide) are superposed and actively interact. In the pair alcohol–water the latter component is a stronger acid than the alcohol, and suppresses dissociation thereof; at the same time the undissociated alcohol molecules act as a base towards the water, displacing the equilibrium towards formation of hydroxide ions. The net result is that the concentration of alkoxide ions and the rate of addition of alcohol to acetylene fall. The accompanying absorption of acetylene which is observed in several cases is probably due to "vinylation" of water[36,40]. Another secondary reaction involving water,

$$HC{\equiv}CH + H_2O + NaOH \rightarrow CH_3COONa + H_2:$$

is known[56]. According to a patent[57] almost pure hydrogen and sodium acetate in 96% yield can be obtained in this way.

Towards phenol water acts as a base and an ionising agent: it intensifies dissociation of the phenol, thereby increasing the concentration of phenoxide ions, which ultimately facilitates vinylation. Alcohols are also capable of filling the function of water as an ionising agent and a proton-acceptor in the vinylation of phenols[40,53-55]. In our view a similar explanation can be put forward for the favourable influence of water and alcohols in the vinylation of thiols[40,53-55,58] and also for the possibility of using t-butyl alcohol as the medium in the vinylation of alcohols[39]. The favourable influence of dioxan and *N*-methylpyrrolidone on vinylation[59] is probably due primarily to their increased ability to dissolve acetylene; however, being strong proton-acceptors, these solvents should further also strengthen the acid–base dissociation of the substrate.

The rate of vinylation falls appreciably on passing from a primary to a tertiary alcohol[10,60,61]. Since the nucleophilic character of alkoxide ions increases in the same sequence, this observation appears at first glance to contradict the mechanism of nucleophilic vinylation. This is seemingly not only a matter of steric hindrance to activation. According to the scheme of concerted addition, the rate of vinylation depends both on the nucleophilic character of the alkoxide ion and on the ability of the medium to donate protons. The latter is known to fall from a primary to a tertiary alcohol.

Although the above mechanism of simultaneous *trans*-addition provides an acceptable explanation for most of the features of nucleophilic vinylation, nevertheless it is probably an extremely crude approximation, and cannot claim to be universally applicable. In particular, it is difficult with its aid to provide any satisfactory explanation of the known dependence of the reaction velocity on the cationic portion of the catalyst[40,45] (though this applies to all other mechanisms of vinylation). It has been suggested[40] that nucleophilic attack at the triple bond is preceded by attack by the cation with formation of an "acetylene–cation" complex compound. In any case, it is now clear that all the variety of modifications and variants of the reaction of vinylation cannot be forced into the framework of any one scheme.

2. Field of Application

In principle the reaction does not extend merely to those functionally substituted alcohols and phenols which contain structural units sensitive to alkalis and to heat. Compounds which have not yet proved susceptible to direct vinylation include in particular unsaturated aliphatic alcohols (the higher unsaturated alcohols possibly constitute an exception[62]). The main reason preventing direct vinylation in unsaturated alcohols may be supposed to be their prototropic isomerisation into the corresponding carbonyl compounds. In a kinetic study[45] of the vinylation of allyl alcohol (together with other alcohols) in the presence of sodium hydroxide as catalyst, the reaction velocity was measured from the absorption of acetylene, but it is not clear whether allyl vinyl ether was isolated in the pure form. The vinylation of the but-2-enyl and allyl monoethers of ethylene glycol[63] is apparently not accompanied by isomerisation of the radical. Tertiary ethylenic alcohols, with which the final stage of isomerisation (conversion into the α-ethylenic alcohol, and then into a carbonyl compound) is excluded, can probably be vinylated under the conditions of the Favorskii–Shostakovskii reaction with preservation of the molecular skeleton. In general, of course, the position of the double bond need not necessarily be maintained here. In this connection patent information[64] on the preparation of the vinyl ether of *p*-menth-1-en-8-ol (together with the vinyl ethers of other mono- and poly-cyclic terpene alcohols) by vapour-phase vinylation over basic catalysts is not without interest. In the case of acetylenic alcohols isomerisation may be supplemented by intramolecular and intermolecular "self-vinylation".

3. Alcohols having Oxygen-containing Functions

(*a*) Alkoxyalkanols. Alcohols containing alkoxy-groups (monoethers of glycols) are smoothly vinylated under ordinary conditions with the formation of alkoxyalkyl vinyl ethers[4,63,65,66]. Monoalkyl ethers of hydrobenzoin have been successfully vinylated[67-69]. Furfuryl vinyl ether has been obtained[70] in 45% yield by the vinylation of furfuryl alcohol in aqueous medium; the reaction is more successful in the absence of solvents (yield of the ether 68.7%[71]). The presence of water proved necessary in the vinylation of guaiacol[72] and other alkoxyphenols[73].

(*b*) Glycols. In the vinylation of 1,2- and 1,3-glycols, cyclic acetals[74,75]—products of the isomerisation[76] of monovinyl ethers—are usually present in the reaction mixture. The vinylation of ethylene glycol is accompanied[23] by the formation of other unsaturated products, boiling at 150–195°C, of undetermined structure. However, this has not been confirmed in later investigations. With propyne[77] ethylene glycol gives exclusively 2,4-dimethyl-1,3-dioxolan under the conditions of vinylation.

A patent stated[78] that vinyl ethers of ethylene glycol could be obtained by passing a mixture of acetylene and the glycol vapour over heated metals (calcium, magnesium, barium, copper, aluminium), peroxides, or salts on carriers. The preparation was reported[33,34] of vinyl ethers of glycols (the monovinyl ether of ethylene glycol and the

divinyl ethers of ethylene, diethylene, and triethylene glycols) by the action of acetylene diluted with an inert gas on the diols in the presence of alkaline catalysts under pressure. Vinylation forms the basis of a process for the manufacture of the divinyl ether of butane-1,4-diol[4,79]. The synthesis of the divinyl ether of triethylene glycol has been described in a thesis[12]. A process which has been patented[80] for the production of monovinyl ethers of ethylene glycol, trimethylene glycol, and diethylene glycol is based on the rapid removal of the resulting ethers from the reaction zone by means of excess of acetylene or an inert gas. Shostakovskii et al.[81] accomplished the synthesis of the monovinyl ethers of ethylene, propylene, tetramethylene, diethylene, and triethylene glycols under pressure. The vinylation of butane-1,4-diol in tetrahydrofuran gives a 52% yield of the monovinyl ether[82]. Monovinyl ethers can be obtained[83] by vinylating glycols in the liquid phase at normal pressure and a temperature of 100°C with simultaneous removal of the reaction products. Some information has been published[45] on the kinetics of the vinylation of butanediol and diethylene glycol. The synthesis of vinyl ethers of diethylene glycol has been discussed also by Zimmerman et al.[84]

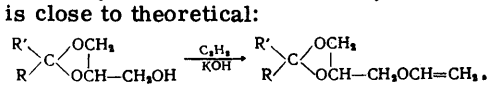
Qualitative assessment indicates that ease of vinylation increases in the sequence from ethylene glycol through diethylene glycol to triethylene glycol[85]. The exhaustive vinylation of triethylene glycol yields as secondary products vinyl ethers of ethylene and diethylene glycols and also 2-methyl-1,3-dioxolan. The vinylation of diethylene glycol is accompanied by the formation of vinyl ethers of ethylene glycol and 2-methyl-1,3-dioxolan. These facts indicate cleavage of the ether bonds during the reaction. Acetylene probably plays an active part in this secondary process. During the vinylation of diethylene glycol partial conversion of the monovinyl ether into an eight-membered cyclic acetal has been noted[86].

A simple apparatus has been developed[87] for the continuous preparation of vinyl ethers of glycols at atmospheric pressure. Continuous synthesis of acetaldehyde is accomplished by subsequent hydrolysis of the vinylation products. This scheme forms the basis of a new industrial method for manufacturing acetaldehyde via the vinyl ethers[88-91]. An interesting and successful attempt has been made to produce vinyl ethers (including those of glycols) by the direct use—instead of free acetylene—of calcium carbide in aqueous medium[92,93] under conditions of alkaline catalysis. A process for preparing the divinyl ethers of quinol, resorcinol, catechol, and trimethylquinol has been investigated[94]. The mono- and di-vinyl ethers of hydrobenzoin and isohydrobenzoin[69,95,96] and of anthraquinol[97] and the divinyl ether of bishydroxyphenylpropane[98] have been obtained.

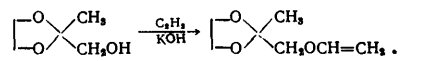
(*c*) Polyhydric alcohols. The early work on the vinylation of glycerol showed[23,75,99] that the yields of mono- and di-vinyl ethers could be controlled by varying the concentration of acetylene, and with excess of the latter exhaustive vinylation could be accomplished. The authors assumed that under these conditions the trivinyl ether of glycerol could be obtained in 90% yield. Subsequent refinement of these investigations by Shostakovskii et al.[20,21,100] has established, however, that a substance which is formed under these conditions in ~ 63% yield is actually 2-methyl-4-vinyloxymethyl-1,3-dioxolan, while the yield of the trivinyl ether of glycerol does not exceed 10%. American workers have reached a similar conclusion[59]. They synthesised the trivinyl ether of glycerol in up to 50% yield by a special method[59] ensuring a considerable excess concentration of acetylene in the reaction zone and brief contact between the reactants, *N*-methylpyrrolidone being used as solvent. The vinylation of glycerol has been accomplished in dioxan with the use of a three- to four-fold excess of acetylene in the presence of potassium butoxide[20,21,100]. Under these conditions 2-methyl-4-vinyloxymethyl-1,3-dioxolan and the trivinyl ether of glycerol were obtained in 43% and 25–28% yields respectively. The mono- and di-vinyl ethers of glycerol could not be isolated. Preparation of a monovinyl ether of glycerol has been reported[4,75], as also that of monoalkenyl ethers of glycerol[101,102].

The first communication on the vinylation of pentaerythritol and trishydroxymethylethane was made by Atavin[103]. In the latter case[104] 5-hydroxymethyl-2,5-dimethyl-1,3-dioxan, 2,5-dimethyl-5-vinyloxymethyl-1,3-dioxan, and 2,2-bisvinyloxymethylpropanol were isolated. Under the same conditions a diacetal and 2-methyl-5,5-bisvinyloxymethyl-1,3-dioxan were obtained from pentaerythritol[105]. A 22% yield of a divinyl ether of pentaerythritol has been synthesised in aqueous medium[106]; further vinylation of the product in the absence of water yielded a tetravinyl ether (60–70%) and 2-methyl-5,5-bisvinyloxymethyl-1,3-dioxan (30–40%). On vinylating pentaerythritol in alcohol, only a tetravinyl ether was isolated[107].

(*d*) Partial ethers of polyhydric alcohols. The vinylation of 1-alkoxypropane-2,3-diols[20,21,108] gives 4-alkoxymethyl-2-methyl-1,3-dioxolans and 1-alkoxy-2,3-divinyloxypropanes. 2,2-Dialkyl-4-hydroxymethyl-1,3-dioxolans are vinylated at a lower temperature (110–120°C) than are monohydric alcohols[109]. The yield of vinyl ethers is close to theoretical:



Several compounds of this type have been reported previously without detailed description[4-6]. Cyclic ketals of acetol are vinylated without complication[110]:



The preparation of mono-, di-, and tri-vinyl ethers of cellulose has been reported[111]. Subsequently only the corresponding acetals could be isolated[112] on vinylation of the same carbohydrate. Recently cellulose has been vinylated in aqueous dioxan[113]. Tetrahydrofuran was used as solvent for the vinylation of starch[114]. Vinylation of mannitol[115] gave only a low yield of its triacetal. A 10 to 15-fold excess of acetylene is necessary in order successfully to suppress isomerisation during the vinylation of polyhydric alcohols[116]. In this way a tetravinyl ether of α-methylglucoside and vinyl ethers of cellulose were obtained in yields of 65–80%. The vinylation of mono- and di-acetyl derivatives of α-glucose, α-galactose, mannitol, sorbitol, and dulcitol has been accomplished. In all cases it was reported that the completely vinylated ethers were isolated[117]. When acetylene reacts with poly(vinyl alcohol)[118] in aqueous alkali, not more than 6 mole % of the hydroxyls are etherified.

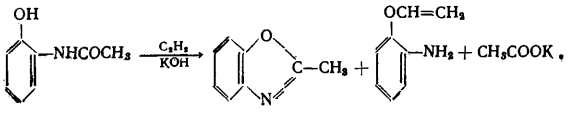
(*e*) Alcohols having other oxygen-containing functions. Very brief mention has been made[4,6] of the production of vinyl ethers of partial acetates of ethylene glycol and glycerol in the presence of salts of organic acids. The yields are not given, the boiling point serving as the only characteristic of the ethers. The reaction is accompanied by active redistribution of acyloxy-groups. Among hydroxy-compounds having other oxygen-containing functions, phenolic ketones have been successfully

vinylated[98]. The reaction conditions are analogous to the synthesis of the vinyl ethers of alkylated and arylated phenols[119,120]. Naphthyleneglycollic acid is converted[121] under conditions of vinylation into a mixture of mono- and di-vinyl ethers, the latter of which has been obtained also directly from acenaphthenequinone.

4. Nitrogen-containing Alcohols

(*a*) Amino-alcohols. Vinyl ethers of hydroxyethylamines have been obtained[31-35] in the presence of basic catalysts at 80–250°C. The conditions for the vinylation of aliphatic alcohols are too severe[122,123] for aminoalkanols. The best results are obtained by conducting the reaction in benzene, with an alkoxide of the corresponding alcohol as catalyst. Complete and partial vinyl ethers of bis- and tris-hydroxyethylamines have been synthesised[124]. An apparatus in which a gas–liquid emulsion is produced by means of a stirrer has been proposed[125] for the preparation of trisvinyloxyethylamine. In such apparatus vinylation can be conducted over a wide range of pressures (2–12 atm). Decrease in pressure and the presence of moisture impair the yields of vinyl ethers. Kinetic investigations (with bis-2-hydroxyethylamine in t-butyl alcohol and an initial acetylene pressure of 19.5 atm)[44] indicate that the order of the reaction with respect to the amino-alcohol varies from the first to zero as the concentration of the latter changes. Methods in the mathematical planning of experiments have been used in the kinetic study of the vinylation of trishydroxyethylamine[126]. The vinylation of phenylaminoethanol in the presence of caustic potash in butanol yields phenylaminoethyl vinyl ether[4]; under similar conditions but in the presence of cadmium acetate[127] *N*-phenyloxazolidine is formed.

(*b*) Aminophenols. Various aminophenols[128-133] and hydroxydiphenylamines[132,134] have been subjected to vinylation, the expected vinyl ethers being obtained in all cases. Vinylation is promoted by the presence of 15–20% of water based on the weight of the aminophenol[128]. The corresponding vinyl ethers have been synthesised by the vinylation of phenolic acetanilides[135], the reaction being effected in dioxan medium in the presence of 20–25% of caustic potash. The vinyl ether of *o*-hydroxyacetanilide was not isolated, owing to cyclisation and saponification of the original phenol:



(*c*) Nitrophenols. The possibility of the direct vinylation of *p*-nitrophenol was probably first shown in a kinetic study[40] of the vinylation of substituted phenols. The preparative vinylation of *o*-, *m*-, and *p*-nitrophenols is accomplished[136,137] in aqueous dioxan in the presence of cadmium acetate. Caustic potash and zinc acetate proved to be less effective catalysts (the yield of ethers did not exceed 2.5–3.5%). The *para*-isomers are most readily vinylated (at 145–150°C), the successful vinylation of *m*- and *o*-nitrophenols requiring temperatures of 175–185°C. Halogenated nitrophenols (2-chloro-4-nitrophenol, 2,6-dichloro- and 2,6-dibromo-nitrophenols) require temperatures of at least 180°C for vinylation, this being due[136] to steric hindrance by the *ortho*-substituents.

5. Mercapto- and Alkylthio-alkanols

Shostakovskii et al.[138] investigated the reaction between acetylene and 2-mercaptoethanol, and obtained a 70–75% yield of 2-vinylthioethanol, which clearly illustrates the greater reactivity of the thiol group than of hydroxyl towards vinylation:

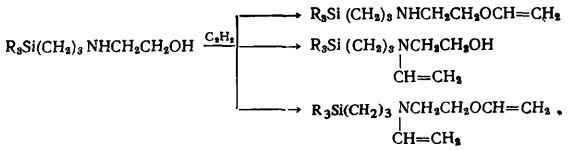
$$HOCH_2CH_2SH + C_2H_2 \xrightarrow[90-105^\circ]{20\%\ KOH} HOCH_2CH_2SCH{=}CH_2.$$

Further vinylation under more severe conditions (120 to 135°C) yields the diether.

The vinylation of 2-ethylthioethanol[139] gave a 40–60% yield of ethylthioethyl vinyl ether. The vinylation of thiodiglycol[140,141] involves complications, and only partly follows the usual scheme: there is a very vigorous competing process, yielding vinyl ethers of 2-mercaptoethanol. Experiments in the absence of acetylene, under otherwise similar conditions, did not yield such ethers. This proves that their formation was not a consequence of dehydration of the thiodiglycol. It is possible that acetylene plays an active part in cleaving the carbon–sulphur bond. It is not excluded that rupture of this bond during vinylation is common to 2-hydroxyalkyl sulphides, although work on the vinylation of 2-ethylthioethanol[139] and 2,2-dialkylthiopropanols, in which only the normal reaction products were isolated[142], would appear not to support this hypothesis. The vinylation of 1-thienylcarbinols in dioxan in the presence of potassium hydroxide yields the corresponding vinyl ethers[143].

6. Silicon-containing Alcohols

γ-Organosilicon alcohols can be vinylated[145] by the Favorskii–Shostakovskii method. The highest yields (65–68%) are obtained[146] at 150–160°C and acetylene pressures of 15–20 atm in the presence of potassium ethoxide. Under these conditions tertiary γ-silicon-containing alcohols are not vinylated[147]. Ethylenic and acetylenic tertiary γ-silicon-containing alcohols are cleaved at the SiC≡C bond during the reaction, with the formation of hexaalkyldisiloxanes. The vinylation of α- and β-silicon-containing alcohols in the presence of potassium hydroxide and alkoxides entails breakdown of the initial compounds[147]. Trialkylvinyloxysilanes can be obtained by vinylating trialkylsilanols[148] in the presence of potassium silanoxide in dioxan medium at 65–70°C. The vinylation of trialkylsilylpropylaminoethanols[149] yields three different products:



In view of the reported[5] unsuccessful attempts at the vinylation of primary and secondary aliphatic amines, the structures of the latter two products perhaps require refinement.

7. Halogenated Alcohols and Phenols

The literature probably contains no example of the direct vinylation of halogenated alcohols: the obstacle is their sensitivity (especially of 1,2- and 1,3-halogenohydrins) to the action of bases. An exception is 2,2,2-trifluoroethanol, which is 90% converted into the vinyl ether

on being vinylated (17% potassium hydroxide at 135–150°C for 10 h) under pressure in an autoclave[150].

Halogenated phenols undergo vinylation without appreciable complication[151,152]. The vinyl ethers of monochloro-(fluoro)-, 2,4-dichloro-, 2,4,6-trichloro-, pentachloro-, and pentafluoro-phenols have been obtained in good yields[153]. Replacement of caustic potash by zinc acetate permitted the synthesis also of the vinyl ethers of 2,4,6-tribromo- and chloronitro-phenols, these phenols being unstable in an alkaline medium. The vinyl ethers of *o*-chloro-, *p*-chloro-, 2,4-dichloro-, 2,4,6-trichloro-, and pentachlorophenols have been prepared[4] by vinylation with acetylene diluted with nitrogen in the presence of zinc and cadmium acetates. The ability of halogenated phenols to undergo vinylation is directly dependent on their acidity[151,152]: fluorophenol is most easily vinylated, and bromo- and chloro-phenols with greater difficulty. These results contradict kinetic data[39,154], and are probably explained by the differing stability of phenols under the conditions of vinylation.

III. ELIMINATION OF THE ELEMENTS OF A HALOGEN HALIDE FROM HALOGENATED ETHERS

In spite of the greater lability of halogen in 1-halogenoethyl ethers (substitution and detachment takes place by a unimolecular mechanism) and the relative accessibility[155,156] of these compounds, they are considerably more rarely used than are 2-halogenoethyl ethers for the synthesis of functional ethers, owing to their instability. The vinyl ethers of allyl and prop-2-ynyl alcohols have been obtained[157] in this way, as also those of mono- and di-methylethynylcarbinols. The effectiveness of the scheme

$$CH_3CH(OR)_2 \xrightarrow{BCl_3} CH_3CHClOR \xrightarrow{(CH_3)_3N} \left[\begin{matrix} CH_3CHOR \\ | \\ {}^{+}N(CH_3)_3 \end{matrix}\right] Cl^- \xrightarrow{100-120^\circ C} CH_3{=}CHOR + N(CH_3)_3 \cdot HCl$$

is due to the use of boron trichloride at the stage of formation of the α-chloro-ether. 2-Chloroethynyl vinyl ether is formed[158] when 1,2′-dichlorodiethyl ether is heated in diethylaniline at 80–85°C. 1-Bromo-2-vinyloxyethylene has been prepared[158] under similar conditions:

$$CH_3CHClCHBrCH_2Br \rightarrow CH_2{=}CHOCH{=}CHBr.$$

α-Silicon-containing vinyl ethers have been obtained[159] by dehydrochlorination of 1-halogenoethyl ethers of the corresponding alcohols:

$$R_3SiCH_2OCHClCH_3 \xrightarrow{-HCl} R_3SiCH_2OCH{=}CH_2.$$

Conditions for the dehydrohalogenation of 2-halogenoethyl ethers have been discussed in detail in a monograph[156]. The reaction goes with considerably greater difficulty than in the cases of 3-halogenoalkyl ethers and alkyl halides. The 2-halogenoethyl ether is usually distilled over excess of solid caustic potash or caustic soda. The peculiar resistance of β-halogeno-ethers to dehydrohalogenation deserves more than mere mention. The process is undoubtedly bimolecular, so that the main factor here is not the lability of the halogen, which has hitherto been stressed[156], but that of the α-hydrogen atom (with respect to the oxygen), which is the primary object of attack by the nucleophile. In view of the polarity of the $O{\leftarrow}C^{\delta+}$ bond, detachment of a proton from the OCH_2 group should apparently be facilitated, whereas actually it is strongly hindered. It may be supposed that there occurs in the $O{-}CH_2$ fragment a special interaction, consisting in partial overlapping between the orbitals of the C–H bonds and those of the lone pairs of electrons of the oxygen atom (*p*–σ conjugation):

$$\left[-O-CH_2 \leftrightarrow -O^+{=}C- \leftrightarrow -O^+{=}C-\right]$$

(with H^- on the C–H bonds and H on the carbon).

2-Chloroethyl vinyl ether is obtained by the dehydrochlorination of bis-2-chloroethyl ether (Chlorex)[160–162], dioxan and small amounts of divinyl ether and acetaldehyde being formed as byproducts[163]. The production of 2-chloroethyl vinyl ether by the pyrolysis of 2-chloroethoxyethyl acetate has been reported[164]. The complete dehydrochlorination of Chlorex provides a convenient route for obtaining divinyl ether itself[165–167]. 2-Bromoethyl vinyl ether has been prepared from bis-2-boromethyl ether[168]. Examples are known of the preparation of an allyl vinyl ether via allyl 2-bromoethyl ether[169,170]. α-Substituted alkyl vinyl ethers have been prepared[171,172] by means of the scheme

$$CH_2{=}CHOR \xrightarrow{Br_2} CH_2BrCHBrOR \xrightarrow{R'MgX} CH_2BrCH(R')OR \xrightarrow[KOH]{-HBr} CH_2{=}C(R')OR\ (80\%).$$

Vinyl ethers of β-silicon-containing alcohols have been synthesised by dehydrochlorination[173]:

$$R_3SiH + CH_2{=}CHOCH_2CH_2Cl \rightarrow R_3SiCH_2CH_2OCH_2CH_2Cl \xrightarrow[350-400^\circ]{KOH} \rightarrow R_3SiCH_2CH_2OCH{=}CH_2\ (75\%).$$

The vinyl ether of glycidol has been prepared by dehydrochlorinating the corresponding 2-chloroethyl ether[174]:

$$ClCH_2CH_2OCH_2CH(O)CH_2 \xrightarrow[200^\circ]{NaOH} CH_2{=}CHOCH_2CH(O)CH_2.$$

Aryl 2-halogenoethyl ethers are considerably more easily dehydrohalogenated[72,153,175]. This can be explained in terms of the above considerations by the part played by the lone electron pairs of the oxygen atom in conjugation with the benzene ring, so that the effect of *p*–σ conjugation with the α-C–H bonds is weakened.

Certain fluorinated vinyl ethers can be synthesised as follows[176]:

$$CH_2{-}CH_2(O) + ROH \rightarrow HOCH_2CH_2OR \rightarrow ClCH_2CH_2OR \xrightarrow{-HCl} CH_2{=}CHOR,$$

where R = CH_2CHFCl, CH_2CF_3, $CH_2C_2F_5$, $CH_2C_3F_7$. Fluorinated alkenes have been used for the same purpose[177]:

$$HOCH_2CH_2OH + F_2C{=}CFCl \xrightarrow{Na} HOCH_2CH_2OCF_2CHFCl \xrightarrow{P/I_2} \rightarrow ICH_2CH_2OCF_2CHFCl \xrightarrow[CaO]{NaOH} CH_2{=}CHOCF_2CHFCl.$$

The series of reactions

$$ROH + COF_2 \xrightarrow{100-120^\circ} ROCOF \xrightarrow{SF_4} ROCF_3 \xrightarrow[C_2H_5OH]{KOH} CH_2{=}CHOCF_3,$$

where R = $ClCH_2CH_2$, $BrCH_2CH_2$, has been proposed[178] for the preparation of trifluoromethyl vinyl ether. The same route has been used to synthesise[178] dichlorovinyl trifluoromethyl ether $CCl_2{:}CHOCF_3$ from trichloroethanol.

Divinyl ethers of *gem*-diols (divinyl acetals) have been obtained by dehydrochlorination of the corresponding 2-chloroethyl acetals[179–181]. Unsymmetrical alkyl 2-chloroethyl acetals have similarly been used[179,180] for the synthesis of α-alkoxylated vinyl ethers (alkyl vinyl acetals) $CH_3CH(OR)OCH{:}CH_2$. Formaldehyde alkyl 2-halogenoethyl acetals $ROCH_2OCH_2CH_2X$ (where X = Cl, Br) treated with potassium hydroxide at 350–400°C yield[182] alkoxymethyl vinyl ethers $CH_2{:}CHOCH_2OR$.

In the case of chloroacetaldehyde bis-2-chloroethyl acetal all three possible vinyl ethers can be isolated[183]. Elimination occurs with greatest difficulty in the aldehyde

part of the molecule, where, according to the ideas discussed above, the single β-hydrogen atom (relative to the halogen) under attack by bases is able to interact by means of its σ-bond with the *p*-electrons of the two oxygen atoms at once. As a consequence its proton mobility is considerably restricted.

Dehydrochlorination has been applied also to cyclic acetals of glycerol chlorohydrin[184]. Chloroacetaldehyde acetals of glycols, glycerol, glycerol chlorohydrin, diethylene glycol, pentaerythritol, mannitol, and sorbitol do not split off hydrogen chloride on treatment with caustic potash in butanol, but form the corresponding acetals of butoxyacetaldehyde[185]. Dehydrochlorination takes place only in the presence of potassium t-butoxide.

IV. VINYL EXCHANGE

Vinyl ethers[186-192] and esters[193-197] are able to exchange their vinyl groups with alcohols in the presence of mercury salts:

$$ROCH{=}CH_2 + R'OH \xrightarrow{Hg^{2+}} ROH + R'OCH{=}CH_2$$

where R = alkyl or acyl. The reaction makes it possible to obtain vinyl ethers containing functional groups which are unstable in the presence of bases. The catalyst is usually mercury acetate or sulphate, while the vinylating agent is an alkyl vinyl ether[186-191], phenyl vinyl ether[192], or vinyl acetate[193-195,197].

The mechanism of exchange is complicated and has not been finally elucidated. The concept of π-complexes explains activation of the vinyl ether, but not the actual act of vinyl migration. It appears paradoxical that a vinyl ether and an organic acid (or alcohol) can coexist in the presence of mercury salts, which are among the most active catalysts of electrophilic addition. It is probable that the hydroxy-component which is formed combines with excess of the vinylating agent to produce the corresponding acetal or acylal.

Vinyl exchange involving vinyl acetate has been explained[197] by dissociation to yield a mercury–acetylene complex and acetic acid:

$$CH_2{=}CHOCOCH_3 \overset{Hg^{2+}}{\rightleftharpoons} [C_2H_2 \cdot Hg^{2+}] + CH_3COOH.$$

According to Watanabe and Conlon[189], vinyl ethers first add the catalyst at the multiple bond:

$$Hg(OAc)_2 \rightleftarrows HgOAc^+ + AcO^-$$

$$HgOAc^+ + ROCH{=}CH_2 + R'OH \rightleftarrows \begin{matrix} RO \\ R'O \end{matrix}\!\!>\!CHCH_2HgOAc + H^+$$

$$\begin{matrix} RO \\ R'O \end{matrix}\!\!>\!CHCH_2HgOAc + ROCH{=}CH_2 + R'OH$$

$$\downarrow\uparrow$$

$$\left[\begin{matrix} RO \\ R'O \end{matrix}\!\!>\!CHCH_2-\right]_2 Hg + HOAc$$

$$\downarrow\uparrow$$

$$\begin{matrix} RO \\ R'O \end{matrix}\!\!>\!CHCH_2HgOAc + R'OCH{=}CH_2 + ROH$$

However, kinetic investigations using isotopes[198] indicate that vinyl exchange catalysed by mercury salts does not involve the intermediate formation of mercury–acetylene complexes or intermediate acetoxymercuration, and therefore a mechanism of direct substitution has been suggested[198].

Vinyl transetherification is widely used for the preparation of functional alkoxyethylenes. Vinyl ethers of several diols have been obtained[187,191,197]. The vinylation of the methyl ester of glycollic acid has been reported[197]. Various vinyl ethers have been used[189,190] for the vinylation of ethylcellulose, allyl, methylallyl, and chloroallyl alcohols, ethylene chlorohydrin, ethylene cyanohydrin, 2-nitropropanol, and 4-hydroxypentan-2-one. Boiling divinylcarbinol in excess of ethyl or isobutyl vinyl ether with mercury acetate and sodium acetate yields[199] the vinyl ether $(CH_2:CH)_2CHOCH:CH_2$. Phenyl vinyl ether has been successfully used[192] for vinylating 2-naphthol, *p*-phenylphenol, and quinol with mercury acetate as catalyst. American workers[200] have obtained the vinyl ethers of phenol, *p*-cresol, and 2,6-dichlorophenol in yields of 80–100%, using divinylmercury as vinylating agent. Polyfluorinated vinyl ethers have been synthesised[201] by the transetherification of vinyl acetate with fluorinated alcohols. The vinyl transetherification of the methyl and ethyl ethers of hydrobenzoin with butyl vinyl ether has been investigated[69,202]. When salicylic acid is treated with vinyl acetate in the presence of mercury acetate, only a cyclic acylal (2-methyl-4-oxobenzo-1,3-dioxan) can be isolated[203].

V. SYNTHESES OF VINYL ETHERS BASED ON THE REACTIONS OF FUNCTIONAL GROUPS IN SUBSTITUTED VINYL ETHERS

The chief obstacles in the way of accomplishing such reactions are the difficult accessibility of functional vinyl ethers capable of further modification involving the functional substituent and the great reactivity of the vinyloxy-group itself. Mild conditions are usually required, and *electrophilic* reagents are then usually unsuitable. Nevertheless, these methods possess great synthetic possibilities.

1. Monovinyl Ethers of Glycols

Until quite recently only a few isolated examples were known of the synthesis of functional ethers from monovinyl ethers of glycols[76,204-208]. After a technically practicable route had been found for synthesising 2-vinyloxyethanol at atmospheric pressure, in the course of the development and industrial exploitation of a mercury-free technology for producing acetaldehyde via vinyl ethers of glycols[21,91], the widespread use of this compound in organic synthesis actually became possible.

Researches carried out during recent years[209] have enabled certain general rules to be formulated for the selective modification of functional fragments of a vinyl ether, and have shown that hydroxylated vinyl ethers may become a new, readily available source of polyfunctional monomers.

New unsaturated diethers were obtained by treating the sodium derivatives of monovinyl ethers of glycols with prop-2-ynyl bromide[210,211]:

$$CH_2{=}CHORONa + BrCH_2C{\equiv}CH \rightarrow CH_2{=}CHOROCH_2C{\equiv}CH.$$

Vinyloxyalkoxyalkynols have been synthesised[212,213] by the reaction

$$CH_2{=}CHOROCH_2C{\equiv}CH + R'R''C{=}O \rightarrow CH_2{=}CHOROCH_2C{\equiv}CCR'R''OH.$$

This reaction has since been applied to other examples[214]. Dehydration of the products[213] yields vinyl ethers containing

an enyne bond system in the alkoxy-radical. Propynyloxyalkyl vinyl ethers react[215,216] with trimethylchlorosilane, both as its sodium and as its magnesium bromide derivative, to form trimethylsilylpropynyloxyalkyl vinyl ethers:

$$CH_2{=}CHOROCH_2C{\equiv}C\,(Na)\,MgBr + ClSi(CH_3)_3 \rightarrow CH_2{=}CHOROCH_2C{\equiv}CSi\,(CH_3)_3.$$

The corresponding reaction with triethyltin chloride yields triethylstannylpropynyloxyalkyl vinyl ethers[217]. Trialkylstannylalkynyl vinyl ethers are obtained by the reaction of alkynyl vinyl ethers containing a terminal acetylenic group with hexa-alkyldistannoxanes and trialkylstannyloxyalkanes[218].

The behaviour of propynyloxyalkyl vinyl ethers under the conditions of the Mannich condensation has been studied[219,220], and dialkylaminobutynyloxyalkyl vinyl ethers have been synthesised:

$$CH_2{=}CHOROCH_2C{\equiv}CH + CH_2O + HNR_2' \rightarrow CH_2{=}CHOROCH_2C{\equiv}CCH_2NR_2'.$$

The same scheme has been since used[221] to synthesise the ether $CH_2:CHOCH_2CH_2C:CCH_2N(C_2H_5)_2$. Potassium t-butoxide in t-butyl alcohol converts propynyloxyalkyl vinyl ethers into the corresponding allenes[222] $CH_2:CHOROCH:C:CH_2$. Successive treatment of vinyloxyethyne with lithamide in liquid ammonia and with butyl bromide[158] converts it into 1-vinyloxyhexyne in 60% yield.

The cyanoethylation of monovinyl ethers of glycols is accompanied[223-225] by the formation of β-vinyloxyalkoxypropionitriles $CH_2:CHOROCH_2CH_2CN$. When these compounds are reduced with lithium tetrahydroaluminate[226], the expected aminoalkyl vinyl ethers are not formed, but the initial molecule undergoes almost quantitative cleavage at the carbon–oxygen bond in the cyanoethoxy-group:

$$CH_2{=}CHOROCH_2CH_2CN \xrightarrow{LiAlH_4} CH_2{=}CHOROH + CH_3CH_2CH_2NH_2.$$

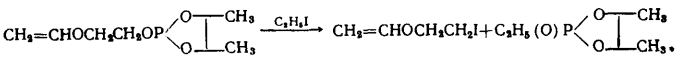
A similar cleavage is observed when the cyanoethoxyalkyl vinyl ethers react with sodium in alcohol[226]. An attempt has been made[227] to prepare the corresponding ketones from these ethers by the Grignard synthesis, but the main reaction products were vinyloxyalkanols and polymeric materials:

$$CH_2{=}CHOROCH_2CH_2CN + R'MgX \rightarrow CH_2{=}CHOROMgX + \text{polymer}.$$

Secondary amines together with paraformaldehyde smoothly aminomethylate monovinyl ethers of glycols, provided that the water evolved is removed azeotropically[225,228,229]. When dialkylaminomethoxyalkyl vinyl ethers interact with alcohols and with thiols[230], the expected addition of the reagents at the vinyl group is not observed, but the carbon–oxygen bond in the aminomethoxy-group undergoes cleavage with formation of the monovinyl ether of the glycol and the corresponding amine.

The monovinyl ethers of mono-, di-, and tri-ethylene glycols react with trimethylchlorosilane to give the corresponding silyl vinyl ethers of the glycols[225,231]. The sodium derivatives of hydroxylated vinyl ethers give with triethyltin chloride almost theoretical yields of triethylstannyloxyalkyl vinyl ethers[225,232,233]. Several vinyl ethers containing an ester group have been synthesised[234] by the interaction of acyl halides with vinyloxyalkanols in the presence of triethylamine. Chlorides of phosphorous acids form with monovinyl ethers of glycols[235,236] or their sulphur analogues[237] a new series of reactive trialkyl phosphites $(AlkO)_2POR$, where R = $CH_2:CHO[CH_2]_2$, $CH_2:CHO[CH_2]_2S[CH_2]_2O$, $CH_2:CHS[CH_2]_2$, etc.

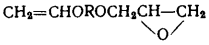
Arbuzov rearrangement of 4,5-dimethyl-2-vinyloxyethoxy-1,3,2-dioxaphospholan in the presence of ethyl iodide yields 2-iodoethyl vinyl ether[238]:



A quantitative yield of dialkyl vinyloxyalkyl phosphorothionates has been obtained[239] by the reaction

$$CH_2{=}CHOCH_2CH_2OP(OC_2H_5)_2 \xrightarrow{S} CH_2{=}CHOCH_2CH_2O(S)P(OC_2H_5)_2.$$

A detailed investigation has been made[240] of the reaction of monovinyl ethers of glycols with epichlorohydrin, and a series of glycidyloxyalkyl vinyl ethers



have been synthesised. Excess of the hydroxylated component favours the formation of a divinyl ether of the structure

$$CH_2{=}CHOROCH_2CH(OH)CH_2OROCH{=}CH_2$$

by a secondary reaction involving the glycidyl fragment. Subsequent cleavage of the oxide ring by means of thiols, amines, metal derivatives of acetylenes, and organochlorosilanes provides a ready method for obtaining the corresponding substituted vinyl ethers[241,242].

2. Halogenated Vinyl Ethers

Halogenoalkyl vinyl ethers possess no less potentialities for the synthesis of functionally substituted alkoxyethylenes, although 2-chloroethyl vinyl ether still remains the only one which is available. Before the start of systematic investigations on vinyl ethers of halogenated alcohols[243,244] there were a few examples of the use of 2-chloroethyl vinyl ether for the preparation of vinyl ethers containing functional substituents (the reactions with alkoxides[245], benzonitrile[246], *N*-substituted 2-trifluoromethylphenothiazines[247], and trialkyl phosphites[248]). It would be of great interest for organic synthesis to obtain a Grignard reagent from halogenoalkyl vinyl ethers. However, the only known attempt in this direction[168], based on 2-bromoethyl vinyl ether, was unsuccessful, this ether being found to decompose into acetylene and ethylene on treatment with magnesium. Similar breakdown was observed[168] on interaction with metallic sodium.

Investigations of nucleophilic substitution of the chlorine atom in 2-chloroethyl vinyl ether[244] have confirmed that, in alcoholic solutions of alkoxides, the latter forms around 30% yields of 2-alkoxyethyl or 2-aryloxyethyl vinyl ethers. The course of the reaction is similar in liquid ammonia with but-3-ynol[249], obtained directly in the reaction medium from ethylene oxide and sodium acetylide. Alk-1-ynes, in the form of their sodium derivatives, are alkylated by 2-chloroethyl vinyl ether in liquid ammonia[250], but the rate of the reaction is fairly low. Replacement by an alkylthio- or arylthio-group takes place considerably more easily[244,251], and treatment with sodium sulphide yields the divinyl ether of thiodiglycol[244]. The reaction of 2-chloroethyl vinyl ether with secondary amines has been used[252] as a basis for a convenient method of synthesising 2-dialkyl(aryl)aminoethyl vinyl ethers of diverse structure. Treatment of 2-chloroethyl vinyl ether with sodium iodide in acetone resulted in replacement of the chlorine atom by iodine[244]. 2-Iodoethyl vinyl ether alkylates tertiary

amines with formation of the corresponding vinyloxyethyltrialkylammonium salts[244], and on treatment with potassium fluoride in diethylene glycol[253] is converted into 2-fluoroethyl vinyl ether. It has been proposed[254] to use vinyl ethers of halogenated phenols for the synthesis of aryl vinyl ethers containing alkyl and alkoxyl groups.

3. Nitrogen-containing Vinyl Ethers

Use of the divinyl ether of bishydroxyethylamine for the aminomethylation of acetylene[255], alcohols[255,256], and thiols[256] opens up a simple path to various classes of nitrogen compounds containing a vinyloxy-group—$R_2C{:}CH$, $RC{:}CR$, $RC{:}CCH_2OH$, $RSCH_2CH{:}CH_2$, etc., where R = $CH_2N(CH_2CH_2OCH{:}CH_2)_2$.

On treatment with vinyl acetate the vinyl ether of aminoethanol and the divinyl ether of bishydroxyethylamine form[257] the corresponding *N*-acetyl derivatives. With methyl chloroacetate the divinyl ether of bishydroxyethylamine gives methyl *NN*-bisvinyloxyethylaminoacetate $(CH_2{:}CHOCH_2CH_2)_2NCH_2COOCH_3$.[258] Methyl *β-NN*-bisvinyloxyethylaminopropionate[258] has been prepared from the divinyl ether of bishydroxyethylamine and methyl acrylate:

$$(CH_2{=}CHOCH_2CH_2)_2NH + CH_2{=}CHCOOCH_3 \xrightarrow{100^\circ} (CH_2{=}CHOCH_2CH_2)_2NCH_2CH_2COOCH_3.$$

The addition of the vinyl ether of aminoethanol to methyl methacrylate has also been reported[259].

In the course of a study of the cycloaddition of dialkylketens to vinyl ethers[260] it was noted that initially the vinyl ether of aminoethanol undergoes vigorous acylation at the amino-group.

Vinyloxyalkylcyanamides[261,262] are formed by reaction between aminoalkyl vinyl ethers and a cyanogen halide:

$$CH_2{=}CHOCH_2CH_2N(R)H + NCHal \rightarrow CH_2{=}CHOCH_2CH_2N(R)CN,$$

where R represents methyl, allyl, or cyclohexyl. The resulting ethers react with dicyandiamide to form[262] *N*-methyl-*N'*-vinyloxyethylmelamines. Treatment of aminoalkyl vinyl ethers with potassium cyanate[263] in acidified water (pH > 6.8) yields vinyl ethers of hydroxyalkylated ureas. Analogous compounds have been synthesised by reaction between urea and aminoalkyl vinyl ethers. Treatment of isocyanatoalkyl vinyl ethers with aqueous ammonia and with aziridine[264,265] also yields the corresponding vinyl ethers containing a ureido-group:

$$CH_2{=}CHOCH(CH_3)CH(CH_3)N{=}C{=}O \xrightarrow{NH_3} \begin{cases} \rightarrow CH_2{=}CHOCH(CH_3)CH(CH_3)NHCONH_2 \\ \rightarrow CH_2{=}CHOCH(CH_3)CH(CH_3)NHCO\text{-}NH \end{cases}$$

Acylation of aminophenyl vinyl ethers with acid chlorides has been used[266] to synthesise vinyloxyanilides of various acids, as well as bis-*p*-vinyloxyphenylurea and isopropyl *m*- and *p*-vinyloxyphenylcarbamates. Reaction between ammonium dialkyl phosphorodithioates and *p*-chloroacetamidophenyl vinyl ether yields[266] *OO'*-diethyl *S*-*p*-vinyloxyphenylcarbamoylmethyl phosphorothiolothionate $p\text{-}CH_2{:}CHOC_6H_4NHCOCH_2SPS(OC_2H_5)_2$.

The acylation of vinyl ethers of aminophenols by means of anhydrides of organic acids have also been described[135,267]. Interation of vinyl ethers of aminophenols with acrylaldehyde and with furfuraldehyde forms the basis of proposed methods for the preparation of vinyl ethers of alkenyl- and furyl-aldiminophenols[268,269].

Whereas dialkyl phosphorodithioates add readily at the double bond in aryl vinyl ethers containing no substituents of basic character in the ring[266,270], aminophenyl vinyl ethers form salts $[CH_2{:}CHOC_6H_4NH_3]^+[(RO)_2PSS]^-$ in the analogous reaction[271]. Reduction of vinyl ethers of nitrophenols in alkaline medium yields divinyl ethers of azo- and azoxy-phenols[272,273].

4. Divinyl Ethers

The addition of hydrogen chloride to divinyl ether itself takes place in stages, and ultimately 1-chloroethyl vinyl ether can be isolated in yields up to 60%.[158,165] When divinyl ether interacts with carbon tetrachloride[274] it is difficult to retard the reaction in any way substantially at the first stage, the yield of tetrachloropropyl vinyl ether being only 17%. Divinyl ether undergoes the Diels–Alder reaction with hexachlorocyclopentadiene[275,276] and with anthracene[277]. Two adducts are formed, the yields of which depend on the proportions of the components and the temperature of the reaction. Some divinyl ethers of glycols have been subjected to hydroxylation[278,279], but monoadducts have not been isolated.

Hemiacetals (1-hydroxyalkyl vinyl ethers) $RCH(OH)OCH{:}CH_2$ have been obtained[280] by interaction between divinylpropanals and mercuric oxide in the presence of mercury acetate in aqueous–alcoholic medium.

Promising routes for the synthesis of functionally substituted vinyl ethers from divinyl ethers will probably be opened up by the investigation of reactions of homolytic addition occurring preferentially at one of the vinyloxy-groups.

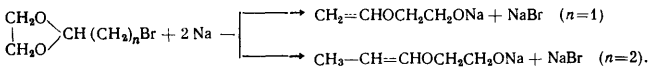
VI. CATALYTIC ELIMINATION IN A SERIES OF FUNCTIONAL ACETALS

The preparation of vinyl ethers containing functional substituents by eliminating one alcohol molecule from an appropriate acetal has not yet become widely used. The initial functional acetals are in general difficultly accessible compounds, being in several cases most easily obtained actually from vinyl ethers. Another reason lies in the conditions of the reaction[281–285], which are often either severe or altogether inapplicable with certain functional groups. The method is used mainly for the preparation of 2-substituted vinyl ethers[283,286–288] of the type AlkCH:CHOAlk which cannot be obtained by direct vinylation. Nevertheless, the literature contains several examples of the use of this method for obtaining vinyl ethers of functional alcohols (allyl vinyl ether[289,290], ethyl vinyl ether of ethylene glycol[282], a polyfluorinated vinyl ether $CH_2{:}CHOCH_2CF_3$,[291,292] alkynyl vinyl ethers[293,294]). When unsymmetrical alkynyl ethyl acetals undergo cleavage[214], the relative proportions of ethyl vinyl and alkynyl vinyl ethers depend on the structure of the radical, the yield of acetylenic ether increasing in the sequence $CH_2C{:}CH$ (5%) < $CH_2CH_2C{:}CH$ < $CH(CH_3)CH_2C{:}CH$ (70%). From this we conclude that the acid-catalysed pyrolysis of unsymmetrical acetals takes place predominantly with elimination of the most electronegative radical and formation of the more stable carbonium ion $[CH_3CHOR]^+$.

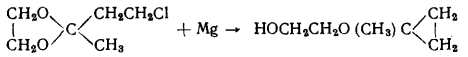
VII. OTHER METHODS

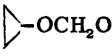
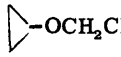
1. Interaction of Acetals of α-Halogenoaldehydes with Metals

This method[295] is seldom used in practice, and then mainly for the preparation merely of vinyl ethers of monohydric alcohols[286,296,297]. Among functional vinyl ethers it is probable that only hydroxylated αβ-unsaturated ethers are obtained in this way[76,298,299]:



Feugeas and Normant[300] reported that the action of metallic magnesium in ether on the cyclic acetal of α-chloroacetone (2-chloromethyl-2-methyl-1,3-dioxolan) gave not an organomagnesium compound but the 1-methylvinyl monoether of ethylene glycol. The same reaction with cyclic acetals of β-halogeno-ketones yields not a vinyl ether but an ether of cyclopropanol:



Cyclic acetals of αγδξ-halogeno-ketones react similarly with metallic magnesium, forming 2-hydroxyethyl ethers of the corresponding cyclic alcohols. Apparently Hill and Pidgeon[298] were dealing not with 2-methyl- and 2-ethylvinyl ethers of ethylene glycol but with the corresponding cyclopropanol derivatives , .

2. Reaction of Alkoxides of Functional Alcohols with Vinyl Halides

The possibility of extending the Butlerov reaction[301] to functional alcohols has been demonstrated by the synthesis of vinyl ethers of ethylene glycol by heating (to 80–90°C) vinyl chloride with sodium glycolates under pressure[302]. It is not excluded that the process may be only formally a case of nucleophilic substitution, the reaction actually involving an intermediate stage in which free acetylene is formed[6].

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Irkutsk Institute of Organic Chemistry, Siberian Division, USSR Academy of Sciences