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αβ-UNSATURATED ETHERS AND THEIR ANALOGUES IN REACTIONS OF DIENE SYNTHESIS

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1. INTRODUCTION

αβ-Unsaturated ethers, such as simple vinyl ethers, cyclic unsaturated ethers of the dihydrofuran and dihydropyran type, alkoxydienes, and alkoxyacetylenes, represent a special group of unsaturated compounds as regards their combination of chemical properties. Similar properties are possessed by their sulphur analogues, the αβ-unsaturated sulphides, and by ketens. The compounds of this group are distinguished by high reactivity in a variety of conversions which proceed by an ionic mechanism, mainly with electrophilic reagents. From the standpoint of chemical structure these compounds are distinguished by the presence at the double bond of an electron-donating substituent (–OR or –SR), which determines the special nature of the polarisation of the double bond.

The most characteristic representatives of this group of compounds are the vinyl ethers, in the properties of which appear most distinctly and uniquely the fundamental features of the chemical properties and structure possessed by the unsaturated ethers and their analogues.

Among the reactions of the vinyl ethers which take place by an ionic mechanism are hydrolysis, addition of alcohols and organic acids, hydrogen halides and halogens, polymerisation and copolymerisation. Most of the reactions of vinyl ethers are catalysed by mineral acids and by Lewis acids, that is, by electrophilic reagents. At the same time they are completely stable to the action of nucleophilic reagents—alkalis. Vinyl ethers do not react with alkali metals[1]. Many reactions which proceed by a radical mechanism are not characteric for alkyl vinyl ethers. In sharp contrast to the ease with which ionic (cationic) polymerisation of alkyl vinyl ethers takes place is their passivity in radical polymerisations[2–5]. Schildknecht and coworkers[4], who made a comparative study of the polymerisation of various unsaturated compounds, divided them into three groups according to the type of

TABLE 1. Classification of the alkene monomers by polarisability type.

First group	Second group	Third group
2-Methylprop-1-ene	styrene	ethylene
Methylbutene	butadiene	vinyl halides CH_2=CHX
α-Methylstyrene	divinyl ether	vinylidene dihalides CH_2=CX_2
2-Isopropenyltoluene	methyl vinyl ketone	vinyl esters CH_2=CHOCOR
Alkyl vinyl ethers	*N*-vinylpyrrolidone	acrylic esters
Methyl vinyloxyacetate CH_2=CH–O–CH_2COOCH_3	*N*-vinylcarbazole	methacrylic esters

polymerisation (Table 1): first group—compounds which polymerise by an ionic mechanism under the action of Friedel-Crafts catalysts at low temperatures but which do not give the usual high-molecular-weight polymers in free-radical or thermal polymerisation; second group—those which polymerise by both an ionic and a radical mechanism; third group—compounds which polymerise by a radical mechanism and give high-molecular-weight polymers in peroxide or thermal polymerisation.

Even by the above criterion alkyl vinyl ethers are sharply distinguished from unsaturated compounds which contain at the double bond such electron-acceptor substituents as carbonyl, carboxyl, an acyloxy-group, halogen, etc. which enter into the third group. In one group with the alkyl vinyl ethers are certain unsaturated compounds which contain electron-donor substituents at the double bond. The existence of an intermediate group of unsaturated compounds is natural. According to polymerisation type, the intermediate group includes not only divinyl ether but also aryl vinyl ethers and alkoxy-dienes, which are capable of both ionic and radical polymerisation[6,7], to which, however, all the ionic reactions of alkyl vinyl ethers are inherent. In addition to high reactivity in relation to various electrophilic reagents, in which they show complete similarity with alkyl vinyl ethers, acetylenic ethers also react with nucleophilic reagents, for example, with amines, by forming addition products at the triple bond[8,9]. Evidently this can be explained by a breakdown in the symmetry of the electron cloud of the carbon atom in the formation of a triple bond and by the exposure of a positive charge, which makes nucleophilic attack possible[10].

In vinyl sulphides, the properties of which are in many respects analogous to those of vinyl ethers, the presence of a sulphur atom brings about a series of peculiarities, which are expressed, in particular, in a duality in their properties, and in a greater variety of chemical conversions. In polymerisation type these compounds can evidently be assigned to the second group, since they readily polymerise by both an ionic and a radical mechanism[11]. Furthermore, the vinyl sulphides generally show considerable activity in radical reactions[12]. Many ionic reactions of keten are extremely close in nature to the reactions of alkyl vinyl ethers[13].

The reaction with acetals discovered by Müller-Cunradi and Pieroh[14] which proceeds by an ionic mechanism is especially specific for αβ-unsaturated ethers. This reaction has now been studied well[15,16] and it has been shown that a great variety of αβ-unsaturated ethers and sulphides, as well as keten, react with acetals[13]. Nevertheless unsaturated compounds with electron-withdrawing substituents, for example, the compounds of the third group in Table 1, which are generally distinguished by high reactivity, were completely incapable of condensing with acetals.

The behaviour of αβ-unsaturated ethers in the reactions of diene synthesis is highly specific. This appears most sharply in the diene condensations with Schiff bases[17-19]. These reactions serve as yet another criterion for the separation of αβ-unsaturated ethers and sulphides into a special group of compounds. Consideration of the behaviour of αβ-unsaturated ethers in diene condensations with a different type of dienophiles allows certain conclusions to be drawn concerning the mechanism of diene synthesis in general.

At the basis of the specifics of chemical properties of the αβ-unsaturated ethers lies a feature of their structure, the investigation of which has been investigated in a series of special physicochemical and spectroscopic studies. Especially interesting results were obtained recently in studying the infrared and NMR spectra of these compounds.

2. STRUCTURE OF THE αβ-UNSATURATED ETHERS AND THEIR ANALOGUES

A feature of the structure of the αβ-unsaturated ethers and their sulphur analogues is the presence of an –OR or –SR group at a double bond. According to the theory of electron displacement[20,21] the –OR and –SR groups exhibit a negative induction effect ($-I_S$), but less than, for example halogen atoms. This is shown clearly from Table 2, which gives the dissociation constants of substituted acetic acids[22]. In accordance with the lower electronegativity of the sulphur atom in comparison with the oxygen atom the –SR group has a smaller induction effect than the –OR group.

On the other hand, the –OR and –SR groups exhibit a positive mesomeric effect ($+M$), greater than the halogen atoms. The mesomeric effect of the –SR group is less than that of the –OR group, in accordance with the rule[20,21] by which within the limits of a given group of the Periodic System the higher the atomic number the less the tendency to form double bonds. The above two factors should evidently determine the static state of the electrons of the double bond of unsaturated ethers and sulphides. Finding the relation of these two effects is of considerable importance.

The orientation of ionic addition of various reagents to αβ-unsaturated ethers leads to the conclusion about the presence of an excess of negative charge at the β-carbon atom. On this basis it could be assumed that on the negative induction effect of the –OR group in these compounds is superposed a positive mesomeric effect and that as a whole this group is an electron donor:

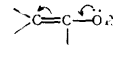


TABLE 2. Dissociation constants of substituted acetic acids.

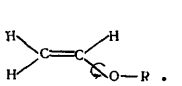
Acid	K
CH_3COOH	$1.855 \cdot 10^{-5}$
CH_3S–CH_2COOH	$1.92 \cdot 10^{-4}$
C_2H_5O–CH_2COOH	$2.50 \cdot 10^{-4}$
CH_3O–CH_2COOH	$2.94 \cdot 10^{-4}$
Cl–CH_2COOH	$1.55 \cdot 10^{-3}$

In recent years the investigation of the NMR spectra of a series of unsaturated ethers has allowed direct proof to be obtained of the existence of increased electron density at β-carbon atoms due to the mesomeric effect of the –OR group, which is expressed in the conjugation of the unshared electron pair of the oxygen atom with the π-electrons of the double bond. Analogous results were also obtained for unsaturated sulphides. Investigation of the ultraviolet and infrared spectra and heats of hydrogenation also suggest the presence of $p-\pi$-conjugation.

In the NMR spectra of alkyl vinyl ethers[23-25] an extremely large chemical shift has been observed for β-protons to the side of higher fields (75–85 Hz) in comparison with ethylene[26]. It has been shown[25] that this effect cannot be due to the anisotropy of the oxygen atom but is the consequence of conjugation of the unshared pair of the electrons of the oxygen atom with the unsaturated system. In methyl vinyl sulphide the shift for the β-protons is considerably less (14–28 Hz). Were the chemical shift of the protons due to the inductive effect of the oxygen and sulphur atoms the picture should be reversed. The observed difference in the chemical shift of the β-protons is explained by the difference in the degree of $p-\pi$-conjugation of the oxygen and sulphur atoms, which is more significant for oxygen. For α-protons the observable difference in the chemical shift corresponds to the order of electronegativity of the oxygen and sulphur atoms. The chemical shifts in methyl vinyl and butyl vinyl ethers are almost the same. Group R does not significantly affect the β shift and evidently does not change the degree of $p-\pi$-conjugation of the oxygen. The oxygen atom acts as a buffer between group R and the double bond. In isopropenyl methyl ether the methyl group decreases the total shift of the two β-protons by 16 Hz, which is considerably below the effect of the methyl group in propene, where there is a general shift of the β-protons by 30 Hz in comparison with ethylene.

Interesting results[27] were obtained in investigating the NMR spectra for the series of substituted ethylenes $CH_2=CHX$, where X = H, CH_3, Cl, OCH_3, CN, and C_6H_5. The existence of a linear relation between the chemical shift of the β-protons and the group dipole moments of substituents X was demonstrated. Parallel curves were obtained for *cis*- and *trans*-β-protons. The results for methyl vinyl ether (X = OCH_3) fit into this relation if it is assumed that the group OCH_3 as a whole is positive in relation to ethylene (dipole moment +1.16 D). This is analogous to *p*-chloroanisole, in which the group dipole moment of the chlorine atom and the OCH_3 group are added together.

Investigation of the vibrational spectra (infrared and microwave) of alkyl vinyl ethers showed that they have a series of features connected with the direct proximity of the ethereal oxygen to the double bond[28-31]. In the region of the C=C stretching vibrations in the spectra of alkyl vinyl ethers the presence of three absorption bands is noted, at 1642 cm^{-1}. On the basis of a consideration of the published data and additional experimental investigations it was shown[28,29] that the presence of these bands is connected with the realisation of rotation isomers:



On the basis of the microwave spectra the difference in the energies of the rotation isomers for butyl vinyl ether was determined. The vibrational spectrum of methyl vinyl ether was investigated in detail[29]. The results of the investigations suggest that the rotation isomers which arise differ in the degree of interaction of the π-electrons of the double bond with the unshared electron pair of the oxygen atom. The bathochromic shift of the absorption band of the double bond of alkyl vinyl ethers which is observable in their ultraviolet spectra[32] (absorption band in the region 1900–2000 Å) in comparison with the double bond of alkenes (absorption band at 1800 Å) can be explained by conjugation. The results of an investigation of the spectra of vinyl sulphides[33] also show the existence of interaction of the sulphur atom with the double bond.

Kistiakowsky and coworkers[34] determined the value of the heat of hydrogenation of certain unsaturated compounds including several vinyl ethers (Table 3). The results obtained show that there is considerable conjugation of CH=C–O–C. This conclusion follows from the heats of hydrogenation of the alkyl vinyl ethers having a mean value between the heats of hydrogenation of unconjugated double bonds, for example, in allyl alcohol, and the heats of hydrogenation of the double bond having an aromatic nature, for example, in furan.

The results of Doliver and coworkers[34] were recently confirmed by calculation of the heat of hydrogenation from measured heats of combustion[35]. The heats of combustion of ethyl vinyl and divinyl ethers compared with the heat of combustion of diethyl ether are:

$$\Delta H^0_c \text{ (diethyl ether, } g) = -657.52 \pm 0.18 \text{ kcal mole}^{-1},$$
$$\Delta H^0_c \text{ (ethyl vinyl ether, } g) = -615.98 \pm 0.22 \text{ kcal mole}^{-1},$$
$$\Delta H^0_c \text{ (divinyl ether, } g) = -578.14 \pm 0.19 \text{ kcal mole}^{-1}.$$

The authors state that conjugation in ethyl vinyl ether is slightly higher than in divinyl ether.

The dipole moments of vinyl ethers[36] (Table 4) differ little from those of the corresponding saturated ethers. Evidently, in the present instance they cannot give any information about the degree of polarisation of the double bond.

Ketens are analogues of the vinyl ethers in the sense that they also contain an oxygen atom at a double bond and in them, just as in the vinyl ethers, conjugation of the unshared electron pair of the oxygen atom with the π-electrons of the double bond is possible, as Ingold first stated[37]. Determination of the dipole moments of the transition in ketens showed that they are considerably (30–40%) lower

TABLE 3. Heats of hydrogenation of unsaturated compounds.

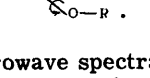
Compound + xH_2	Heat of hydrogenation $\Delta H_{355°K}$, kcal mole^{-1}
$CH_3-C(OC_2H_5)=CH_2+1H_2$	−25.101±100
$CH_3-C(OCH_3)=CH-CH_3+1H_2$	−24.797±200
$C_2H_5O-CH=CH_2+1H_2$	−26.740±60
$CH_2=CH-O-CH=CH_2+2H_2$	−57.236±100
 $+2H_2$	−36.630±120
$CH_2=CH-CH_2OH+1H_2$	−31.45±300

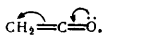
TABLE 4. Dipole moments ($\times 10^{18}$) of the ethers and their analogues.

Compound	Vapour, D	Solution, D
$CH_3—O—CH_3$	1.29	—
$C_2H_5—O—C_2H_5$	1.16	1.22
$C_2H_5—O—C_4H_9$	—	1.20
$CH_2=CH—O—CH=CH_2$	—	1.06
$CH_2=CH—O—C_4H_9$	—	1.25
$CH_2=CH—O—iso\text{-}C_4H_9$	—	1.20
$CH_2=CH—O—C_2H_5$	—	1.19
$HC\equiv C—O—C_2H_5$	—	1.98
$HC\equiv C—O—C_4H_9$	—	2.03
$CH_2=CH—S—CH=CH_2$	—	1.20
$CH_2=C=O$	—	1.45 (gas)
$(CH_3)_2C=C=O$	1.85	—
$(C_6H_5)_2C=C=O$	1.90	—

than in the corresponding ketones[38]. The authors gave the explanation that the effect normal for ketones



is weakened (but not extinguished) by the competing mesomeric effect



Spectrometric studies of keten[39] show the presence of an excess of negative charge at the β-carbon atom.

In the presence of an increased electron density at the β-carbon atom at the double bond, that is, the presence of a nucleophilic centre, $\alpha\beta$-unsaturated ethers and their analogues are distinguished from other types of unsaturated compounds in which the substituents at the double bond have an electron-withdrawing character. On comparing $\alpha\beta$-unsaturated ethers with vinyl halides in which p-π-conjugation is also possible, in the latter it evidently does not appear to the same extent and does not predominate over a more significant induction effect.

The nucleophilic nature of the double bond of $\alpha\beta$-unsaturated ethers explains their high reactivity in relation to electrophilic reagents and the inertness to the action of nucleophilic reagents.

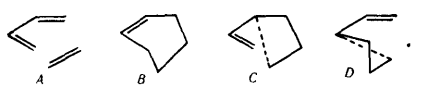
3. MECHANISM OF DIENE CONDENSATIONS

It has now become evident that many of the reactions of diene synthesis which unite the general scheme of addition of a dienophile in the 1,4 position to a diene system cannot be ascribed to any single mechanism both from the viewpoint of the order of combination of the reagents (single- or two-stage) and from the viewpoint of the type of transition of the electrons (homolytic or heterolytic)[40,41]. In support of the single-stage mechanism of a series of diene condensations there are the low values of the pre-exponential factors in the equations for the rate constants of the reactions, approximately 10^{-5}–10^{-6} times the usual rates of collision in gas reactions. In other words, the reactions are characterised by a high negative entropy of activation, which shows that to effect the reactions extremely specific orientation of the reacting molecules is necessary, for example, collision at two points.

In complete agreement with the single-stage mechanism are results[42] which show that acyclic dienes (butadiene) are capable of participating in a diene condensation only after isomerisation into a cisoid conformation. The observance in diene condensations of the principle of *cis*-addition of reagents is also more understandable in single-stage conversion. The mechanisms of the two-stage formation of addition products should provide for additional factors which exclude the possibility of rotation in the product of the first stage of addition[43].

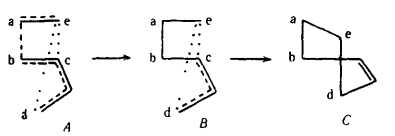
At the same time there are individual instances of diene condensations in respect of which a two-stage mechanism has been established. For example, determination of the change in volume in the formation of a transition state ($\Delta v^{\neq}$) in the dimerisation of isoprene[44] and the diene condensation of 2,3-dimethylbutadiene with butyl acrylate[45] suggested that these reactions are two-stage. It appeared that the transition state is characterised by a significantly greater volume than the reaction products. A single-stage mechanism for the dimerisation of cyclopentadiene was confirmed by the same method[45,46].

According to contemporary views, diene condensations which are stereospecific proceed by the approach of the diene and dienophile molecules which are in parallel planes. The formation of new bonds starts with the overlap of the orbitals of the π-electrons. For a single-stage diene synthesis according to Wassermann[47] the transition state is expressed by a set of resonance structures. For example, structures *A*, *B*, *C*, and *D* represent the transition state for the reaction of butadiene with ethylene:



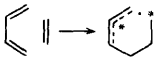
For more complex molecules which contain polar substituents structures which take into account the interaction of specified substituents with unsaturated systems also enter into the transition state.

According to Woodward and Katz[43] the transition state for a two-stage stereospecific diene synthesis can be represented as:



This scheme represents the two-stage mechanism when conversion $B \rightarrow C$ requires an energy of activation. Here the bonds *ed* and *ec* are formed by secondary forces—electrostatic, electrodynamic, and partly exchange forces. When the stage $B \rightarrow C$ of the conversion does not require an energy of activation the bonds *ed* and *ec* are partial and the mechanism stated becomes indistinguishable in practice from a four-centre mechanism.

For a non-stereospecific diene synthesis, transition states of the bipolar ion or biradical type are possible:



There are also contradictory information and opinions concerning the type of electron transition in reactions of diene synthesis. The reactions of the classical diene synthesis (with hydrocarbon diene systems and dienophiles) evidently cannot be related to the heterolytic in external characteristics, since it was shown that the values of the

rate constants and parameters in the Arrhenius equations are almost the same both in the gas phase and in non-polar solvents[40,41]. Moreover, the ideas about heterolytic processes do not agree in many instances with the structural directionality of these reactions[48]. However, it is impossible to classify them as radical reactions, as it was found that they are not catalysed by peroxides[40,41].

Wassermann[47] states that since electrons are indistinguishable there is no sense in speaking of a heterolytic or homolytic transfer of electrons in a four-centre mechanism.

In the mechanism of Woodward and Katz[43] it was assumed that the spins of all the electrons included in the process remain paired all the time. The production of a triplet state under conditions of stereospecific diene synthesis is not very probable[49].

However, it must be noted that the available information on the mechanism of the diene synthesis relates almost exclusively to hydrocarbon dienes and dienophiles. Other types of conversions cannot be ruled out for heterodienes and heterodienophiles, in particular, conversions through bipolar or biradical transition states. Thus, Japanese investigators[50] propose a transition state in the form of a bipolar mesomeric ion for the reaction of octyl vinyl ether with substituted cinnamaldehydes. Henecka[51] states that the formation of ascaridol from α-terpinene and oxygen is a radical reaction. Some authors consider that diene condensations can be brought about by the transfer of electrons into a non-planar six-membered complex, both heterolytically[52,53] and homolytically[51]. We note that apropos of reactions of diene synthesis with hydrocarbon dienes and dienophiles Ingold writes[40] that they proceed predominantly homolytically.

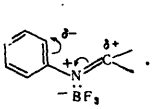
Undoubtedly, for the stereospecific diene synthesis with participation of $\alpha\beta$-unsaturated ethers a tendency to heterolytic transfer of electrons should be more characteristic, considering the unequivocal structural directionality of these reactions and the general uncharacteristic nature of homolytic conversions for this type of dienophile. For example, the condensation of oxygen-containing heterodienes, such as $\alpha\beta$-unsaturated aldehydes, with vinyl ethers always takes place in the same way structurally in accordance with the polarity of the reagents[54,55]. These reactions, moreover, are characterised by the great ease with which they take place and the very high yields of addition products (up to 85%). Alkyl vinyl ethers react with great difficulty with dienes which tend to react preferably by a homolytic mechanism (such as cyclopentadiene)[56]. In their turn these oxygen-containing heterodienes form addition products in very low yields (3–9%) with dienophiles which contain electron-withdrawing substituents at the double bond and tend to radical conversions (such as vinyl acetate, methyl acrylate, methylallyl alcohol, etc.)[57]. Moreover, these condensations proceed structurally despite the polarity of the reagents. Thus the condensation of acrylaldehyde with methyl acrylate leads not to dihydro-3-methoxycarbonylpyran, as might have been expected from the polarity of the reagents, but to dihydro-2-methoxycarbonylpyran. This course of the reaction is explained by the principle of the conjugation of oxygen atoms in the formation of the transition state.

As is well-known, in those instances when the formation of stereoisomers is possible diene condensations proceed stereospecifically with the preferential formation of *endo*-addition products. This was shown by the example of the condensation of cyclopentadiene with maleic anhydride[58,59]. To explain the preferential formation of *endo*-addition products, the principle of the accumulation of multiple bonds in the orientation of reagents in the transition state was advanced. The essence of this principle, which was given quantitative expression in the works of Mousseron and coworkers[60], together with the principle of the conjugation of oxygen atoms (or in the more general form, the principle of the conjugation of unshared electron pairs) is that there are factors other than the polarity of the reagents which are capable of the formation of the transition state. Consideration of the many results on the diene condensation suggests that such a factor can be the general state of charge of the diene system and of the double bond of the dienophile. The action of this factor facilitates the approach of the reagents but does not determine the structural and steric orientation of the components.

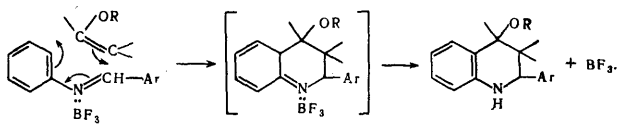
Thus in many of the reactions of classical diene synthesis a diene which does not contain electron-withdrawing substituents is an electron-donor component in relation to the dienophile, whereas the dienophile serves as an acceptor of electrons. This has been confirmed recently by special investigations.

For example, Konovalov[61] studied the reactivity of a series of vinyl and isopropenyl dienophiles which contain electron-withdrawing substituents in reactions of diene synthesis with 2,3-dimethylbutadiene and cyclopentadiene. It was found that the reactivity of these dienophiles increased with decrease in the electron density at the double bond of the dienophile, which was determined as a function of the β-proton chemical shift in the NMR spectrum.

However, as was shown recently[62], there are diene condensations with a reversal of the electronic properties of the components, that is, when the diene serves as the electron-withdrawing component and the dienophile as the electron donor. From this viewpoint the behaviour of alkyl vinyl ethers in the diene synthesis is interesting. Since the double bond of vinyl ethers exhibits a clearly expressed nucleophilic nature, which appears especially sharply in alkyl vinyl ethers, their reactions with dienes should take place the easier the more electron-withdrawing the diene system, and contrariwise will be hindered in electron-donating diene systems. As will be clear from what follows, this position is observed for all the known examples of diene condensations with participation of alkyl vinyl ethers. In addition, such an approach makes it possible to understand the catalysis by Lewis acids of diene condensations of unsaturated ethers and their analogues with Schiff bases[17–19]. As was shown, in the absence of catalysts Schiff bases do not react with unsaturated ethers. And this is understandable, since the quasidiene system formed in this instance by the double bond of the benzene ring and the azomethine group is electron-donating, thanks to the presence of the nitrogen atom. At the same time there are results[63] showing that the diene systems C=C–N=C in oxazoles are capable of reacting with such electron-withdrawing dienophiles as maleic anhydride. In the presence of Lewis acids iminium salts are formed, as was shown[18] by the example of the complex of benzylideneaniline with BF_3. It can be assumed that in this there is strong polarisation of the double bonds:



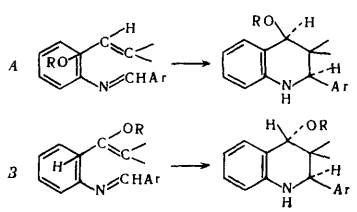
However, besides the above polarisation of the bonds which determine the structural orientation of the components an important factor is that the diene system mentioned acquires electrophilic properties to a high extent. Thanks to this the nucleophilically unsaturated ethers and their analogues react extremely readily with such systems. The reactions begin at room temperature and proceed with considerable evolution of heat giving high yields of addition products:



In addition to conferring electron-withdrawing properties on a diene system a catalyst plays yet another important part. It is already known that to carry out a diene condensation the diene system should have a planar configuration[36]. Moreover it was found[64,65] that in Schiff bases the amine ring is turned through an angle of $\sim 60°$ relative to the plane of the rest of the molecule. This is explained by the competing interaction of the π-electrons of the azomethine group ($\pi-\pi$-conjugation) and the unshared pair of electrons of the nitrogen atom ($p-\pi$-conjugation) with the π-electrons of the aromatic amine ring. During quaternisation of the Schiff base the unshared electron pair is blocked as a result of which it becomes possible to realise the planar configuration of the molecule necessary for the reaction to take place.

Usually only one addition product, or predominantly one, is formed as a result of the condensation. This shows that the reaction is stereospecific.

The structural directionality of the reaction is always determined unambiguously by the polarity of the reagents. The possibility of stereoisomerism under the conditions of single-stage diene synthesis is connected with the different types of orientation of the reagents in the transition state (*A* or *B*):



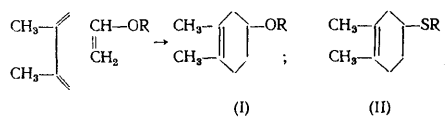
If it is assumed that orientation *A*, corresponding to the principle of the accumulation of unsaturation and unshared electron pairs, is pre-eminent, then the addition products formed predominantly must be considered to be the *cis*-isomers. This also agrees with the observed dependence of the ratio of the isomers on the reaction temperature[19].

Hence the reaction of unsaturated ethers with Schiff bases, which is a new type of diene condensation, is one of the extreme instances of the combination of the electron structures of the dienophile and a diene, namely, the instance when the dienophile exhibits clearly expressed nucleophilic properties and the diene system is electron-withdrawing to a high degree.

4. REACTIONS WITH HYDROCARBON DIENES

Diene systems which do not contain electron-withdrawing substituents exhibit increased electron-donating properties as has been shown by many examples of the reactions of diene synthesis, where they emerge as electron-donating components. Reactions with such dienes evidently have a predominantly homolytic character, which first and foremost relates to dienes not containing strongly polarised double bonds with substituents of electron-donating nature. Dienes such as butadiene, isoprene, 2,3-dimethylbutadiene, etc. easily form addition products with dienophiles containing electron-withdrawing substituents, the double bond in which has a diminished electron density. Thus butadiene and 2,3-dimethylbutadiene form addition products with maleic anhydride in quantitative yields even at room temperature[66].

There are very few examples of the reaction of vinyl ethers with the above hydrocarbon dienes. Apparently, alkyl vinyl ethers are generally incapable of giving addition products with many of these. This can be judged from the fact that in those instances when addition products were obtained, very severe conditions were used and the yields of the addition products were low. Thus, Shostakovskii and coworkers[67] carried out a diene synthesis of n-hexyl vinyl, cyclohexyl vinyl, and phenyl vinyl ethers with 2,3-dimethyl-1,3-butadiene. When the reagents were heated at 220–235°C for 10–12 h addition products were obtained—derivatives of 3,4-dimethylcyclohex-1-ene (I):

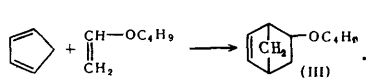


where (I) R = n-C_6H_{13}, C_6H_{11}, C_6H_5; (II) R = C_2H_5, C_6H_5.

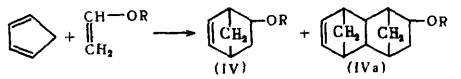
With n-hexyl vinyl ether the yield of addition product was 33.3%. Cyclohexyl vinyl ether (yield of addition product 43.3%) and phenyl vinyl ether (yield of addition product 47%) are somewhat more active. n-Decyl vinyl ether did not give an addition product. Analogous products (II) were obtained with ethyl vinyl sulphide and phenyl vinyl sulphide under milder conditions (175°C, 12 h and 180–185°C, 15 h), the yields being 38.2 and 27.4% respectively.

One of the most active dienes in the reactions of classical diene synthesis is cyclopentadiene, the structure of the molecule of which favours the formation of the transition state. In reactions of diene synthesis cyclopentadiene acts as a donor of electrons. This can explain the extreme ease of reactions with dienophiles which exhibit an electron-withdrawing double bond. For example, methyl vinyl ketone condenses with cyclopentadiene with liberation of heat, by forming an addition product in quantitative yield[68]. On the other hand, alkyl vinyl ethers, as nucleophilic dienophiles, have very weak activity in relation to cyclopentadiene. Reactions take place under severe conditions and give insignificant yields of addition products; in several instances addition products are not formed in general.

Plate and Meerovich[68] first condensed butyl vinyl ether with cyclopentadiene by heating a mixture of the reagents at 200°C for 15 h. This gave 5-butoxybicyclo[2,2,1]hept-2-ene (III) in only 10% yield;



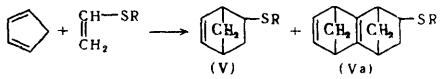
Subsequently Shostakovskii and coworkers[53,69-71] studied the condensation of a series of vinyl ethers with cyclopentadiene. As was shown, the reaction with alkyl vinyl ethers is more difficult and necessitates heating at 180–195°C for 15 h. Under these conditions ethyl vinyl ether did not give an addition product at all and addition products were obtained in low yield from butyl vinyl and cyclohexyl vinyl ethers. Aryl vinyl ethers form addition products in high yields under somewhat milder conditions (heating at 160–170°C for 13 h). It has been found that in the reaction in addition to mono-addition products—ethers of 5-hydroxybicyclo[2,2,1]hept-2-ene (IV)—an insignificant quantity of bis-addition products (IVa) is formed:



(IV) (IVa)

where R = C_4H_9, C_6H_{11}, $C_{10}H_{17}(\beta)$; C_6H_5, C_6H_4-t-C_4H_9.

For aryl vinyl ethers the total yield of the mono- and bis-addition products reached 95%. Vinyl sulphides also give addition products more readily than alkyl vinyl ethers[53,72], derivatives of 5-mercaptobicyclo[2,2,1]hept-2-ene (V) being formed, as well as bis-addition products (Va)



(V) (Va)

where R = C_2H_5, C_4H_9, C_6H_5.

Heating at 160–165°C for 12 h leads to the formation of a mixture of mono- and bis-addition products with a total yield of 72–80%.

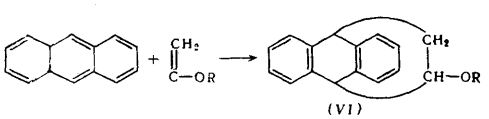
Earlier Alder and coworkers[73] obtained an addition product of cyclopentadiene with *p*-tolyl vinyl sulphide. Prilezhaeva and coworkers[74] state that ethyl vinyl sulphide did not give an addition product with cyclopentadiene at 110°C.

It has been reported[62] that the cyclic unsaturated ether 2,3-dihydrofuran does not form addition products with cyclopentadiene and 9,10-dimethylanthracene.

Shostakovskii and coworkers[71] showed that the reaction of vinyl ethers is stereospecific. In several instances they isolated two isomeric addition products, evidently corresponding to the *endo*- and *exo*-orientation of the reacting components, and showed that their ratio varied with the temperature.

Anthracene, the central ring of which contains an active diene system, reacts rather readily with electron-withdrawing dienophiles. Thus, on boiling anthracene and maleic anhydride in benzene for 3 h, an addition product was obtained in 96% yield[66].

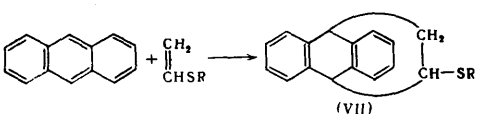
Shostakovskii and coworkers[75] studied the reaction of a series of vinyl ethers and sulphides with anthracene, at 220–240°C for 13–15 h. Phenyl vinyl ether was the most active. At higher temperatures the reaction products resinified, and at lower temperatures the reaction was retarded. Under these conditions addition products (VI) were obtained in yields from 66 to 90% on the anthracene participating in the reaction:



(VI)

where R = C_4H_9, C_6H_{13}, C_6H_{11}, C_6H_5, *m*-$C_6H_4CH_3$, $C_{10}H_{21}$, $C_{10}H_{17}(\beta)$, and $C_{10}H_7(\beta)$.

Condensation of anthracene with vinyl sulphides under analogous conditions at 180°C gave addition products (VII) in yields of ~ 65% on the anthracene undergoing reaction:



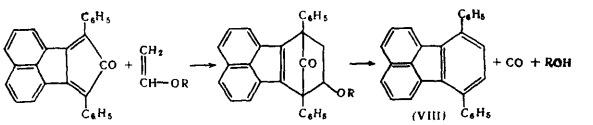
(VII)

where R = C_2H_5, C_6H_5.

Hence here also the electron-donating properties of vinyl ethers and sulphides hinder the reaction of diene synthesis. Note that the authors give the yields of (VI) and (VII) on the anthracene entering into the reaction. Evidently the yields are considerably less than theoretical. For example, for n-hexyl vinyl ether the experimental results show that the yield of addition product is 46% of theoretical, whereas the yield on the anthracene entering into the reaction was 77.6%.

5. REACTIONS WITH SUBSTITUTED HYDROCARBON DIENES

Abramov and coworkers[76-78] studied the reaction of a series of vinyl ethers with various cyclones. These are dienes which contain an electron-withdrawing substituent (the C=O group). The presence of this group should diminish the nucleophilic nature of the diene system, possibly conferring on it to some extent an electrophilic nature. Actually, with electrophilic dienophiles such as maleic anhydride cyclones do not react as readily as cyclopentadiene. The reaction of cyclopentadiene with maleic anhydride starts at room temperature and is exothermic[79,80]. With a cyclone rather prolonged heating of the mixture of reagents is necessary[81]. On the other hand the reaction of cyclones with vinyl ethers takes place more readily than with cyclopentadiene, giving higher yields of addition products under analogous conditions. Thus, ethyl vinyl ether, which did not give an addition product with cyclopentadiene, gave addition product (VIII) in 77% yield with acecyclone[76]. Analogous addition products were obtained with butyl vinyl and phenyl vinyl ethers.

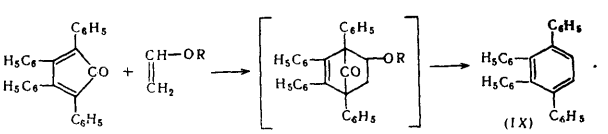


(VIII)

where R = C_2H_5, C_4H_9, C_6H_5.

The reactions take place on heating the reagents in sealed tubes at 180–200°C for 10–15 h, and are accompanied by loss of the *endo*-carbonyl bridge and the alcohol. It has been shown[76] that allyl derivatives and vinyl bromide react with acecyclone with great difficulty.

In the reaction with tetracyclone, carried out under analogous conditions[77] vinyl ethers were used: butyl vinyl, isopentyl vinyl, phenyl vinyl, and 1,2,3-trivinyloxypropane. These reactions take place by the equation:

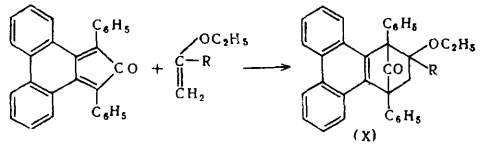


(IX)

In all the reactions 1,2,3,4-tetraphenylbenzene (IX) was obtained in good yield (74–86%).

Addition products of tetraphenylcyclone and acecyclone with ethyl 1-methylvinyl and ethyl 1-phenylvinyl ethers were obtained[78]. These condensations required more prolonged heating (up to 75 h).

Phencyclone reacts more readily than other cyclones with 1-substituted vinyl ethers[78], giving addition products with an *endo*-carbonyl bridge (X)

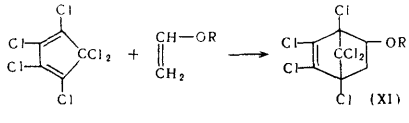


(X)

where R = CH_3, C_6H_5.

Of other dienes with electron-withdrawing substituents only the chloro-substituted dienes, mainly hexachloropentadiene, have been investigated in reactions with vinyl ethers and sulphides. Only one communication about the condensation of chloroprene with ethyl vinyl ether has been published[82], and in this the addition products could not be isolated from the reaction products.

Thanks to the presence of the electronegative chlorine atoms hexachlorocyclopentadiene has a diene system impoverished in electrons and therefore capable of showing electron-withdrawing properties. This can explain the much greater ease with which diene condensations proceed with nucleophilic dienophiles[62], including vinyl ethers. For example, with ethyl vinyl ether[83] hexachloropentadiene gave an addition product—1,2,3,4,7,7-hexachloro-5-ethoxybicyclo[2,2,1]hept-2-ene (XI)—in 36% yield on heating for 6 h at 80–90°C. Under analogous conditions an addition product is also obtained with isobutyl vinyl ether



(XI)

Analogous addition products were obtained with cyclohexenyl ethyl ether[84] on heating at 160°C for 8 h in a sealed tube.

By heating a mixture of phenyl vinyl ether and hexachlorocyclopentadiene at 120–130°C for 2 h, 1,2,3,4,7,7-hexachloro-5-phenoxybicyclo[2,2,1]hept-2-ene was obtained in 72% yield[69].

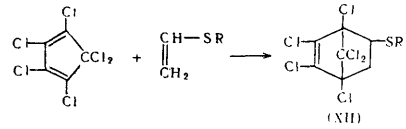
Addition products were also obtained with other aryl vinyl ethers, including naphth-2-yl vinyl and *p*-t-butylphenyl vinyl ethers[70].

Kalabina and coworkers[85] studied the reaction of vinyl ethers of *o*-, *m*-, and *p*-nitrophenols with hexachlorocyclopentadiene. These condensations proceed under more severe conditions in comparison with phenyl vinyl ether (in boiling xylene for 6.5 h) and give smaller yields of the addition products (11–15%).

The condensation of divinyl ether with hexachlorocyclopentadiene takes place[86] at 120°C and leads to 1,2,3,4,7,7-hexachlorobicyclo[2,2,1]hept-2-en-5-yl vinyl ether.

2,3-dihydrofuran reacts with hexachlorocyclopentadiene at an appreciable rate[62], much more rapidly than maleic anhydride.

A series of addition products have been obtained from vinyl sulphides. Thus ethyl vinyl sulphide[74], which did not give an addition product with cyclopentadiene at 110°C, gave one with hexachlorocyclopentadiene at room temperature after 36 days—1,2,3,4,7,7-hexachloro-5-ethylmercaptobicyclo[2,2,1]hept-2-ene in 71% yield. In another study[72] this reaction was carried out at 100–105°C (3.5 h) and then addition product (XII) was obtained in 83% yield:



(XII)

where R = C_2H_5, C_6H_5.

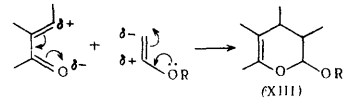
In the same work an addition product of hexachlorocyclopentadiene and phenyl vinyl sulphide was obtained (120°C, 3 h) in 71.5% yield.

In contrast to the electron-withdrawing substituents, electron-donating substituents of the diene system hinder the diene synthesis with vinyl ethers. Thus, furan and 2-methylfuran, which with maleic anhydride form addition products at room temperature in quantitative yields[66], did not give addition products with alkyl vinyl ethers even on heating at 280°C for many hours[87].

6. REACTIONS WITH HETERODIENES

A. Reactions with Oxygen Heterodienes

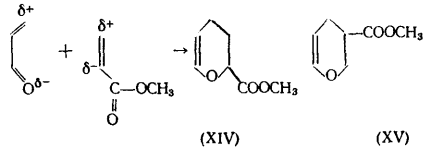
In 1950 Longley and Emerson[88] found that acrylaldehyde and other $\alpha\beta$-unsaturated aldehydes and ketones, on reacting as dienes, readily add vinyl ethers in the 1,4-position, to form the addition products (XIII) in accordance with the polarity of the reagents. For example, with acrylaldehyde they obtained 2-alkoxy-derivatives of dihydropyran:



(XIII)

The reactions were carried out by heating mixtures of the components in a bomb in the presence of a little hydroquinone at 135–200°C for 12–30 h. The yields of addition products were 50–85%.

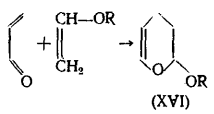
The diene systems of this type contain an electronegative oxygen atom, due to the polarisation of double bonds and imparting an electron-withdrawing character to the system as a whole. By this it was possible to explain the relative ease with which the condensation of such dienes with vinyl ethers is effected. These dienes also react with electron-withdrawing dienophiles, for example, with methyl acrylate[54]. As already stated above, here the reaction proceeds despite the polarity of the reagents and the addition product formed is 2-methoxycarbonyl-3,4-dihydro-2*H*-pyran (XIV) and not 3-methoxycarbonyl-3,4-dihydropyran (XV):



(XIV) (XV)

Hence although the presence of an oxygen atom also confers electron-withdrawing properties on the diene system, this system is capable of reacting also as electron-donating with dienes which exhibit strong electron-withdrawing properties.

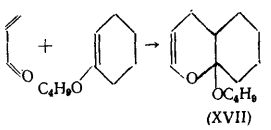
Diene condensations between $\alpha\beta$-unsaturated aldehydes or ketones and vinyl ethers have been studied for many examples[88-91]. In the work mentioned[88] it was shown that acrylaldehyde, on reacting with various alkyl vinyl ethers, forms 2-alkoxy-3,4-dihydro-2*H*-pyran (XVI) in up to 84% yield:



(XVI)

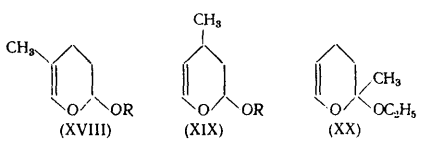
where R = CH_3, C_2H_5, C_4H_9, iso-C_4H_9.

In the reaction with butyl cyclohex-1-enyl ether the addition product obtained was 1-butoxy-2-oxabicyclo[4,4,0]dec-3-ene (XVII):



(XVII)

In the condensation of methylacrylaldehyde and crotonaldehyde with vinyl ethers 2-alkoxy-5-methyl- (XVIII) and 2-alkoxy-4-methyl- (XIX) 3,4-dihydro-2*H*-pyran are formed with yields of up to 87%:

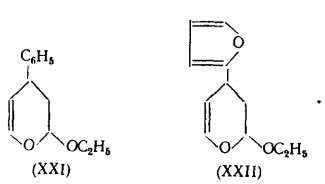


(XVIII) (XIX) (XX)

where R = CH_3, C_2H_5, C_4H_9, iso-C_4H_9.

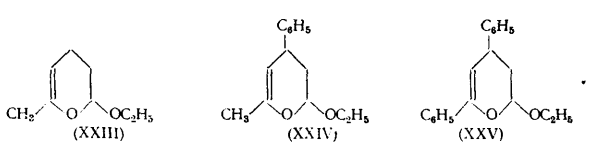
A low yield (25%) was obtained only in the condensation of methylacrylaldehyde with methyl vinyl ether. 2-Ethoxy-3,4-dihydro-2-methyl-2*H*-pyran (XX) was obtained in the condensation of acrylaldehyde with ethyl isopropenyl ether[88].

On condensation with ethyl vinyl ether, cinnamaldehyde and β(furfurylidene) acrylaldehyde give addition products (XXI) and (XXII) in 60–85% yield:



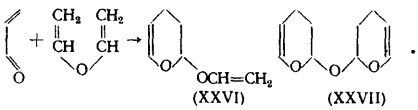
(XXI) (XXII)

On heating methyl vinyl ketone, benzalacetone, and benzalacetophenone with ethyl vinyl ether at 140–200°C for 13–16 h, derivatives of dihydropyran (XXIII), (XXIV), and (XXV) are obtained in yields of up to 75%:



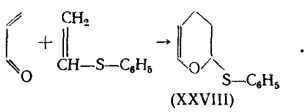
(XXIII) (XXIV) (XXV)

Independently of Longley and Emerson, Smith and coworkers[89] carried out a series of similar condensations, but under somewhat different conditions—they carried out the reaction at higher temperatures and for a shorter time, mainly by heating a mixture of the components without a solvent at 180°C for 1 h. The yields of addition products were as high. In addition, the authors studied the reaction of acrylaldehyde with divinyl ether and showed that here two addition products are formed—mono- (XXVI) and bis- (XXVII) addition products:



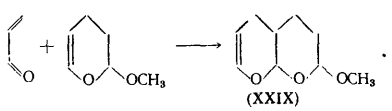
(XXVI) (XXVII)

In addition, addition products of acrylaldehyde with phenyl vinyl ether and phenyl vinyl sulphide were obtained. The latter gave addition product (XXVIII) in 77% yield:



(XXVIII)

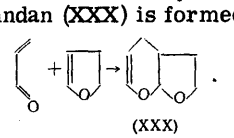
It was shown that the addition product of acrylaldehyde and methyl vinyl ether—3,4-dihydro-2-methoxy-2*H*-pyran—is capable of condensing with a second molecule of acrylaldehyde, giving (XXIX):



(XXIX)

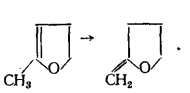
The structure of the addition products was shown by hydrolysis to the corresponding glutaraldehydes, and also by hydrogenation with subsequent hydrolysis of the tetrahydropyrans to 5-hydroxyvaleraldehyde and its derivatives.

Cyclic $\alpha\beta$-unsaturated ethers of the type of 4,5-dihydrofuran and 5,6-dihydropyran[92] under analogous conditions are readily condensed with $\alpha\beta$-unsaturated carbonyl compounds. Thus, on heating in an autoclave (140°C, 16 h) mixtures of 4,5-dihydrofuran and acrylaldehyde, 4,7,8,9-tetrahydro-1,7-dioxaindan (XXX) is formed:

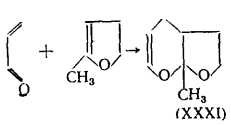


(XXX)

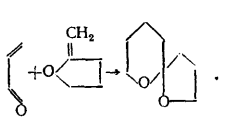
The condensation of 4,5-dihydro-2-methylfuran with acrylaldehyde under the same conditions is complicated by the isomerisation of the unsaturated ether into tetrahydro-2-methylenefuran:



This leads to the formation of two addition products, (XXXI) and (XXXII), in the ratio 7 : 3, with a total yield of 39%:



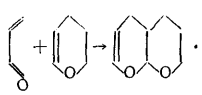
(XXXI)



(XXXII)

Addition product (XXXII) is formed with a yield of 60% in the condensation of acrylaldehyde with pure tetrahydro--2-methylenefuran. The structure of the addition products was shown by hydrogenation and subsequent hydrolysis with a yield of the compounds described.

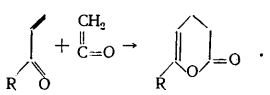
Dihydropyran was less active. On heating it with acrylaldehyde at 140°C for 15 h, Δ^2-octahydro-1,8-dioxanaphthalene (XXXIII) was obtained in only 15% yield:



(XXXIII)

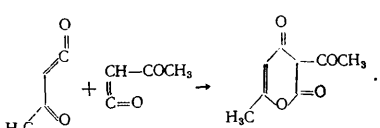
Hydrolysis of (XXXIII) led to 2-(3-hydroxypropyl)glutaraldehyde.

The condensation of a series of $\alpha\beta$-unsaturated carbonyl compounds with keten has been described[93]; these condensations proceed analogously to the reactions of alkyl vinyl ethers, leading to the δ-lactones (XXXIV):



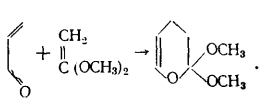
(XXXIV)

The dimerisation of diketen[94] proceeds by a diene synthesis scheme with formation of the addition product (XXXV):



(XXXV)

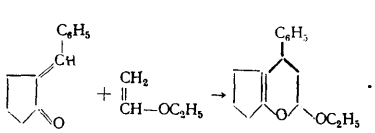
Condensations of a series of $\alpha\beta$-unsaturated aldehydes and ketones with keten dimethyl acetal [1,1-dimethoxyethylene] have been described[95]. With acrylaldehyde at 100°C, 5,6-dihydropyran-6-one dimethyl acetal (XXXVI) was obtained in 70% yield:



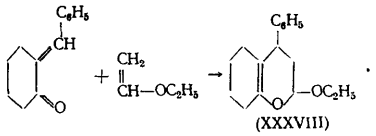
(XXXVI)

The condensation of cinnamaldehyde and benzalacetone with keten dimethyl acetal takes place at a higher temperature (150–200°C), giving the corresponding addition products with yields of 30–60%.

Heterodienes such as cyclic *o*-methyleneketones are also capable of the reactions of the diene synthesis with ethyl vinyl ether. It has been shown[96] that 2-benzylidenecyclopentanone and 2-benzylidenecyclohexanone with ethyl vinyl ether at 160–168°C form the corresponding addition products (XXXVII) and (XXXVIII) with yields of 38–52%:



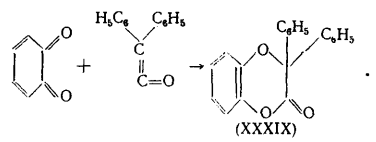
(XXXVII)



(XXXVIII)

The structure of these products was shown by conversion of (XXXVIII) into 4-phenylquinoline. 2-Arylideneindan-1,3-diones condense analogously with ethyl vinyl ether, forming addition products in yields of 43–49%.

Diphenylketen was found capable[97] of being condensed with *o*-benzoquinone, the diene system of which contains two oxygen atoms:

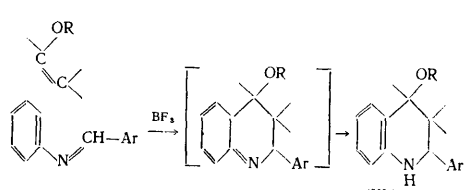


(XXXIX)

B. Reactions with Nitrogen Heterodienes

Almost the only known diene condensations of $\alpha\beta$-unsaturated ethers with nitrogen heterodienes are those with Schiff bases. In 1962 Povarov and Mikhailov [17,98] found that in the presence of boron trifluoride Schiff bases react readily with alkyl vinyl ethers to form addition products according to the diene synthesis scheme. It was shown subsequently that in the reaction with a Schiff base the dienophile can be ethoxyacetylene or keten [18], vinyl sulphide [18,99], the cyclic ethers 4,5-dihydro-2-methylfuran and dihydropyran [100,101], or cyclohexenyl ethyl ether [102]. A wide variety of Schiff bases with various substituents were used as dienes [101,103,104]. It was shown that the anils of non-aromatic aldehydes are also capable of participating in the reaction. For example, addition products were obtained with anils of cinnamaldehyde, citral, and cyclohexanone [101]. The anils of aliphatic aldehydes which are distinguished by a tendency to polymerisation are also capable of condensing with alkyl vinyl ethers at the moment of formation [105]. Apart from BF_3, $AlCl_3$ and $AlBr_3$ are also used as catalysts [19,101]. A diene synthesis between Schiff bases and alkyl vinyl ethers takes place in acetic acid which serves here as the catalyst [106]. The reactions were carried out in solvents such as ether, benzene, and ethyl acetate.

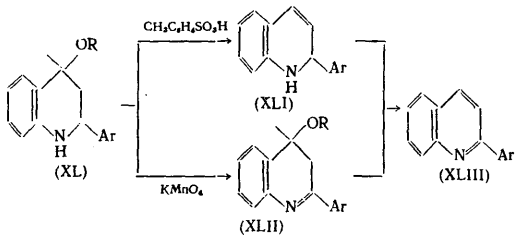
In the reaction of Schiff bases with alkyl vinyl ethers [17,107] derivatives of 4-alkoxy-2-aryl-1,2,3,4-tetrahydroquinoline (XL) are formed:



(XL)

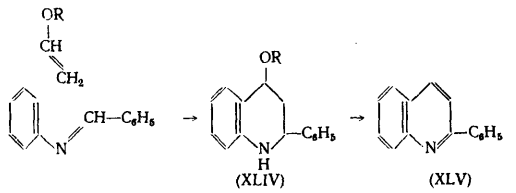
These compounds exhibit extremely weak basic properties; they do not give picrates and do not dissolve in dilute mineral acids. On heating with *p*-toluenesulphonic acid or under the action of oxidants they are converted into the corresponding derivatives of quinoline (XLIII). In the first instance alcohol is lost initially with the formation of 1,2-dihydroquinolines (XLI) and subsequently dehydrogenation takes place. In this part of the 1,2-dihydroquinoline molecule acts as an acceptor of hydrogen. Moreover, in

this example a polymer is formed as a result of the polymerisation of the 1,2-dihydroquinolines (XLI). The yields of quinolines here do not exceed 50%. Under the action of an oxidant ($KMnO_4$ in acetone), the hydrogen atoms in positions 1 and 2 are oxidised initially with the formation of 4-alkoxy-3,4-dihydroquinolines (XLII), then loss of an alcohol takes place readily, and the quinolines (XLIII) are formed with a yield of up to 90%:



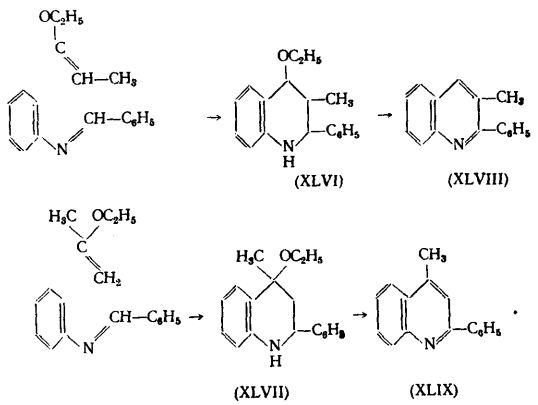
The partial loss of alcohol from addition products (XL) is observed during the reaction and during fractionation, which explains the formation in several instances of an appreciable polymeric residue and the drop in the yield of addition products.

In the condensation of benzylidineaniline with ethyl vinyl, isopropyl vinyl, and butyl vinyl ethers, 4-alkoxy-2-phenyl-1,2,3,4-tetrahydroquinolines (XLIV) were obtained with yields of up to 60%. The structure of the addition products was shown by conversion into 2-phenylquinolines (XLV):

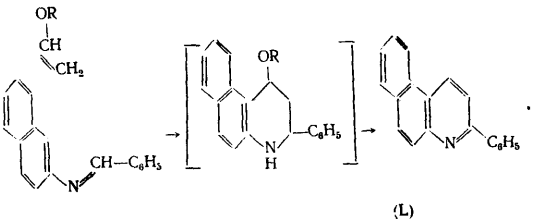


where R = C_2H_5, $CH(CH_3)_2$, C_4H_9.

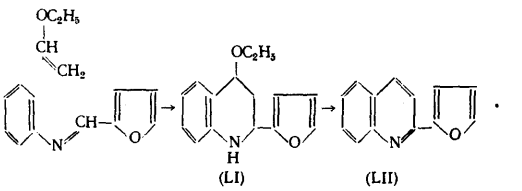
Ethyl prop-1-enyl and ethyl isopropenyl ethers gave respectively 3-methyl- (XLVI) and 4-methyl- (XLVII) 2-phenyltetrahydroquinolines, which were converted further into 3-methyl- (XLVIII) and 4-methyl- (XLIX) 2-phenylquinolines:



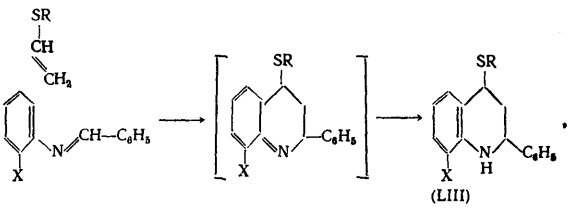
The yield of addition product (XLVII) was low because of the instability of the alkoxy-group at the tertiary carbon atom. The example of these condensations showed the structural directionality of the reaction. Addition products were obtained for alkyl vinyl ethers with a series of substituted benzylidene anils: salicylideneaniline, *o*-nitrobenzylideneaniline, benzylidene-*p*-bromoaniline, benzylidene-*p*-iodoaniline, benzylidene-*p*-anisidine, benzylidene-*p*-phenetidine, *N*-benzylideneanthranilic acid, etc. In several instances the intermediate tetrahydroquinolines (XL) were not isolated but the corresponding quinolines (XLIII) were obtained directly. For example, for benzylidene-2-naphthylamine 2-phenyl benzo[*f*]quinoline (L) is crystallised directly from the reaction mixture:



The condensation of furfurylideneaniline with ethyl vinyl ether led to 4-ethoxy-2-furyl-1,2,3,4-tetrahydroquinoline (LI) from which 2-furylquinoline (LII) was obtained in 36% yield:

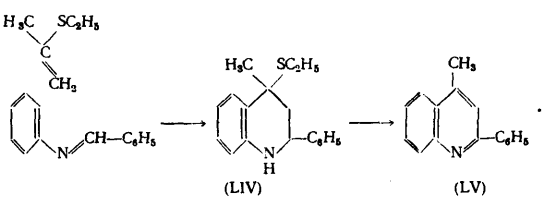


Alkyl vinyl sulphides react no less vigorously than alkyl vinyl ethers with Schiff bases [18,99]. Here the addition products formed are 4-alkylmercapto-1,2,3,4-tetrahydro-2-phenylquinolines (LIII) with yields of 40–60%:



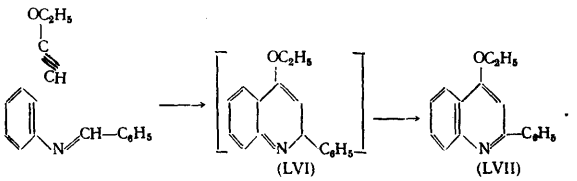
where R = C_2H_5, C_4H_9; X = H, CH_3, CO_2H.

The structure of the addition products was shown by converting them into the corresponding quinolines, which was brought about by heating with *p*-toluenesulphonic acid. This results in the loss of mercaptan and hydrogen. The structural directionality of the reaction was shown by the example of the condensation of benzylideneaniline with ethyl isopropenyl sulphide. The 4-ethylmercapto-1,2,3,4-tetrahydro-4-methyl-2-phenylquinolines (LIV) thus obtained gave, under the action of *p*-toluenesulphonic acid, 4-methyl-2-phenylquinoline (LV):



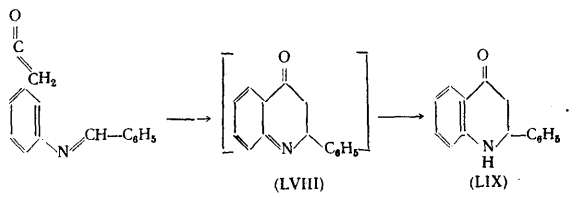
It was shown that the weaker the basicity of the Schiff bases the more readily they react with alkyl vinyl sulphides. Thus the condensation of benzylidene-*p*-anisidine and benzylidene-*p*-phenetidine, the basic properties of which are higher than those of benzylideneaniline, proceeded with difficulty. The only addition products isolated were 6-methoxy- and 6-ethoxy-2-phenylquinolines with yields of 6.6 and 34.7% respectively.

The reaction of ethoxyacetylene with benzylideneaniline[18] leads to 4-ethoxy-2-phenylquinoline (LVII). Addition product (LVI), which is produced initially in accordance with the diene synthesis scheme, is unstable and, on losing hydrogen, is converted into the stable compound (LVII):



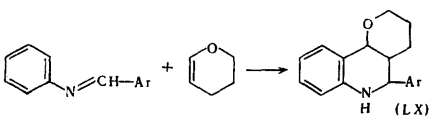
(LVI) (LVII)

In the reaction of benzylideneaniline with keten[18] the addition product (LVIII) which is formed initially is isomerised into 2,3-dihydro-2-phenylquinol-4-one (LIX):



(LVIII) (LIX)

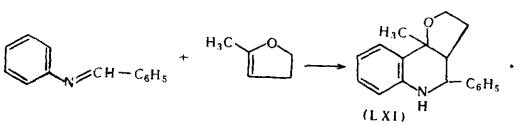
Cyclic ethers, such as dihydropyran and dihydrosylvan, are also capable of being condensed with Schiff bases. Dihydropyran[100] gave 2-aryl-3,4:3′,2′-tetrahydropyrano-1,2,3,4-tetrahydroquinolines (LX):



(LX)

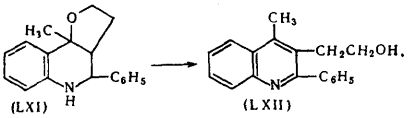
where Ar = C_6H_5, 

An especially active dienophile in relation to Schiff bases is dihydrosylvan, from which a large number of addition products was obtained, the yields reaching 70–80% in many instances. Usually the addition products are stable crystalline substances. Thus with benzylideneaniline[100], 4-methyl-2-phenyl-3,4:3′,2′-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (LXI) was obtained in 81.3% yield:



(LXI)

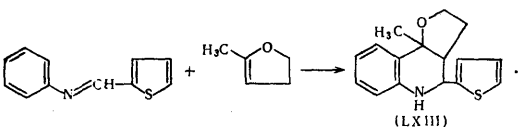
By the action of $KMnO_4$ in acetone[108] on addition product (LXI) the hydrogen atoms in positions 1 and 2 are readily oxidised and the furan ring is opened to form 3-(2-hydroxyethyl)-4-methyl-2-phenylquinoline (LXII):



(LXI) (LXII)

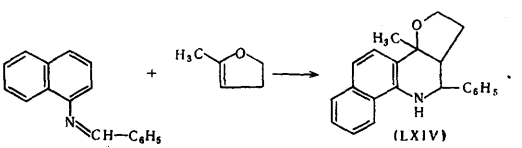
Addition products of dihydrosylvan with various substituted Schiff bases have been obtained[100,101,103,104].

4-Methyl-2-(2-thienyl)-3,4:3′,2′-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (LXIII) was obtained by the condensation of dihydrosylvan with thienylideneaniline[100]:



(LXIII)

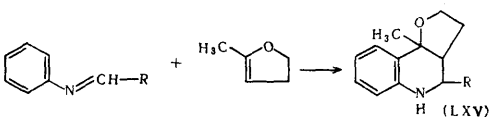
With benzylidene-1-naphthylamine[100] addition product (LXIV) was obtained:



(LXIV)

The reactions of unsaturated ethers with Schiff bases proceed stereospecifically with the formation of a single addition product. Only in certain instances were low-melting isomers isolated in an insignificant amount, their infrared spectra being identical with those of the high-melting addition products[104]. The ratio of the isomers depends on the reaction temperature. At an elevated temperature the amount of the low-melting isomer can become predominant as was shown by the example of the reaction of benzylidene-*p*-methoxycarbonylaniline with dihydrosylvan[19]

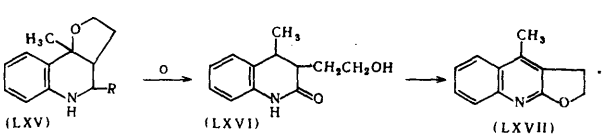
The anils of cinnamaldehyde and citral gave addition products (LXV) containing a vinyl group in position 2:[101]



(LXV)

where R = $-CH=CH-C_6H_5$; $-CH=C(CH_3)CH_2CH_2CH=C(CH_3)_2$.

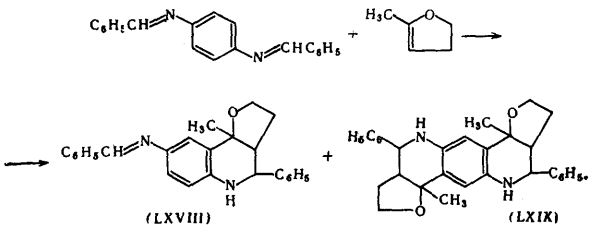
In the oxidation of addition products (LXV) with $KMnO_4$ in both instances 3-(2-hydroxyethyl)-4-methylquinol-2-one (LXVI) was obtained[108], which is readily cyclised under the action of polyphosphoric acid into 4-methyl-2,3:2′,3′-dihydrofuranoquinoline (LXVII):



(LXV) (LXVI) (LXVII)

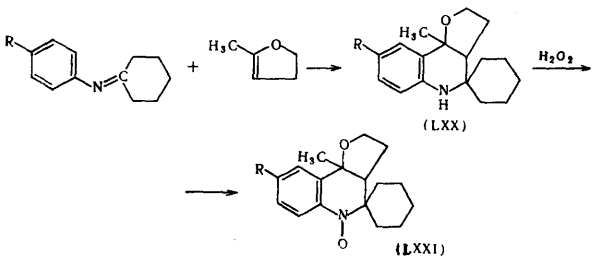
These conversions showed the structure of addition products (LXV), which was also confirmed by infrared spectra.

In the reaction of dihydrosylvan with bis-*N*-benzylidene-*p*-phenylenediamine [19] mono- (LXVIII) or bis- (LXIX) addition products can be obtained, depending on the ratio of the reagents:



(LXVIII) (LXIX)

The reaction of dihydrosylvan with cyclohexanone anils [101,109,110] leads to addition products (LXX), which contain a spirocyclohexyl substituent in position 2. Their oxidation with hydrogen peroxide in the presence of sodium tungstate gave [109-111] stable nitroxide radicals (LXXI):

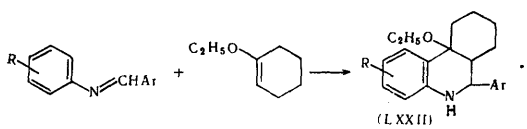


(LXX) (LXXI)

where R = H, OCH_3.

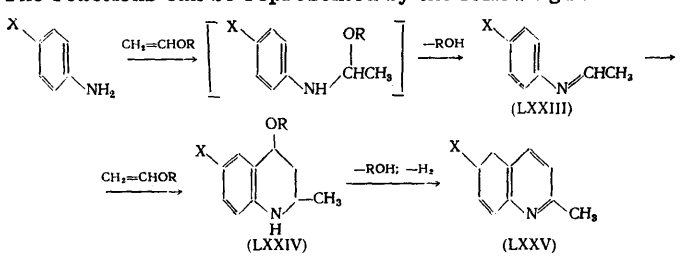
The reaction of cyclohexylidene-1-naphthylamine and cyclohexylidene-2-naphthylamine with dihydrosylvan [109] was used to synthesise 7,8- and 5,6-benzo-derivatives of quinoline of type (LXX), from which stable nitroxide radicals were also obtained.

The reactions of Schiff bases with cyclohex-1-enyl ethyl ether [102] is of special importance since here hydrogenated 9-arylphenanthridines (LXII) are formed:



(LXXII)

Povarov and Mikhailov [105] showed that the anils of aliphatic aldehydes are capable of diene condensations with alkyl vinyl ethers. The reaction conditions were such that the anils of acetaldehyde (LXXIII) reacted with the alkyl vinyl ethers at the moment of formation. This occurred in the reaction of aromatic amines with alkyl vinyl ethers in the presence of boron trifluoride. During this, 4-alkoxy-1,2,3,4-tetrahydroquinaldines (LXXIV) were formed, which under the action of *p*-toluenesulphonic acid were converted into the corresponding quinaldines (LXXV). The reactions can be represented by the following scheme:

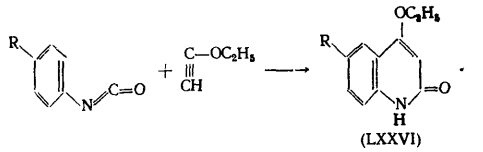


(LXXIII) (LXXIV) (LXXV)

where X = H, OCH_3, Br; R = C_2H_5, C_4H_9.

The reaction usually starts at 30–35°C and subsequently proceeds with liberation of heat. The yields of tetrahydroquinaldines (LXXIV) are 30–50%. In the condensation of 2-naphthylamine with butyl vinyl ether, 5,6-benzoquinaldine was obtained directly.

On other reactions of nitrogen heterodienes with unsaturated ethers the literature contains only a few examples of the condensation of ethoxyacetylene with arylisocyanates [112,113], as a result of which 4-ethoxyquinol-2-ones (LXXVI) were obtained:



(LXXVI)

This reaction has been carried out with phenyl, *p*-tolyl, 1-naphthyl, and *p*-nitrophenyl isocyanates. After 6 months at room temperature an addition product of phenyl isocyanate with ethoxyacetylene was obtained in 42% yield. Resinification occurred at high temperatures.

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REARRANGEMENT OF ACETYLENIC COMPOUNDS WITH PARTICIPATION OF THE π-ELECTRONS OF THE TRIPLE BOND

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INTRODUCTION

After the discovery of the isomerisation of acetylenic hydrocarbons, the rearrangement of acetylenic compounds containing the most diverse functional groups became the subject of many investigations. It was found that acetylenic, vinylacetylenic, and diacetylenic compounds which contain a hydroxyl group, halogens, sulphur, nitrogen, phosphorus, etc. smoothly undergo various rearrangements with the formation of isomeric compounds. Most of these rearrangements are unique, and often the only method of making previously inaccessible new classes of unsaturated alcohols, aldehydes, ketones, and other compounds.

A review of rearrangements of acetylenic compounds has not appeared in the literature, with the exception of Jasiobedzki's article [1] dealing only with the acetylene–allene rearrangement.

In the present article we have tried to collect, and as far as possible, systematise the very interesting and abundant material relating to this subject which has now accumulated.

I. PROTOTROPIC REARRANGEMENT OF ACETYLENIC HYDROCARBONS

During the synthesis of acetylenic hydrocarbons from dihalogenoalkyls Favorskii [2] found that instead of the expected monosubstituted acetylenes disubstituted compounds are obtained. He concluded that under the conditions of the experiment isomerisation of the triple bond along the chain occurred. Subsequently he and his coworkers [3-8] found that various alk-1-ynes isomerise into the