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Condensation of Unsaturated Compounds with Formaldehyde (the Prins Reaction)

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In their review Arundale and Mikeska[1] made a thorough compilation of extensive data on the reaction of olefins with aldehydes and the use of the reaction products in organic synthesis. In recent years numerous papers have appeared in the scientific literature dealing with the mechanism and the chemistry of the Prins reaction and also the possibility of using ion-exchange resins as catalysts, first demonstrated in our laboratory[2].

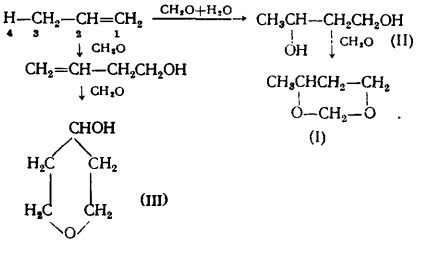
We attempted to review the literature for the period 1953–1965.

1. SYNTHESIS OF 1,3-DIOXANS FROM OLEFINS IN THE PRESENCE OF ACID CATALYSTS

a. Condensation of Olefins with Formaldehyde† in the Presence of Acid Catalysts

In the presence of acid catalysts the main products are 1,3-dioxan and 1,3-glycol. The highest rate of condensation is observed in the reaction of isobutene with formaldehyde. Tertiary olefins with high molecular weights, straight-chain olefins, and also higher aldehydes are less reactive. Apart from the acid catalysts used earlier for the reaction (sulphuric, acetic, hydrochloric, and hypochlorous acids), nitric acid[3] and KU-2 cation-exchange resin[2] have been employed.

In the reaction between propene and formaldehyde investigated by Farberov and coworkers[4,5] optimum conditions are attained at sulphuric acid concentrations of 1–5 wt. %. In the presence of acid of this concentration the main products are 4-methyl-1,3-dioxan (I) (85% yield), butane-1,3-diol (II) (3–5% yield), 1-hydroxytetrahydropyran (III) (7–8% yield), and traces of allylmethanol:



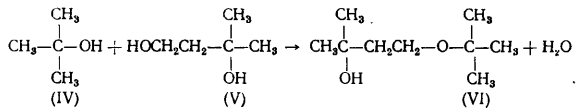
According to the hypotheses put forward by Nesmeyanov and Kabachnik[6], olefins of this type are characterised by

† In some cases formaldehyde is denoted by fa.

the presence of σ, π-conjugation, as a result of which they are capable of two types of reaction, at 1,2- and 1,4-bonds. On the other hand, with isobutene virtually only 1,2-addition takes place (evidently because of the higher rate of this reaction). 4-Acetoxytetrahydropyran was obtained in the condensation of propene in the presence of acetic acid[7]. Isobutene readily condenses with various aldehydes, a complex mixture of products, from which 26 different compounds were isolated, being formed in addition to the main reaction products 1,3-dioxan and 1,3-glycol[8,9].

There exist two views concerning the mechanism of the formation of the dioxan and diol under the conditions of the Prins reaction. In later studies it was assumed that the dioxan and diol may form simultaneously[10]. The mechanism of the Prins reaction will be discussed in detail below.

In the condensation of isobutene with formaldehyde a considerable amount of t-butyl alcohol (IV) forms, and under the conditions of the Prins reaction the latter can react with the 3-methylbutane-1,3-diol (V) produced to give 2-hydroxy-2-methyl-4-t-butoxybutane (VI):



Trenke and Nemtsov[11] were the first to draw attention to this reaction. They hydrolysed the hydroxy-ether obtained in an acid medium both in the presence and in the absence of formaldehyde. t-Butyl alcohol and 3-methylbutane-1,3-diol were obtained in the first case. Hydrolysis in the presence of formaldehyde gave 4,4-dimethyldioxan and t-butyl alcohol; at 98°C the hydrolysis is extensive and rapid in both cases.

Methyldihydropyran and the isomeric methylenetetrahydropyran were also found in the products of the condensation of isobutene and formaldehyde[11,12]. Under the reaction conditions methyldihydropyran reacts with formaldehyde to form a compound containing the pyran and dioxan rings–methyltrioxaperhydronaphthalene[12-14]. In the same papers it is stated that the reaction products contain 4-methyl-4-vinyl-1,3-dioxan and methyldioxanyldioxan.

Under the conditions of the Prins reaction there is also the possibility of the occurrence of the Cannizaro–Tishchenko side-reaction, in which formic acid is formed from formaldehyde and water:

$$2\,CH_2O + H_2O \rightarrow HCOOH + CH_3OH.$$

The loss of formaldehyde by this reaction was investigated by Farberov and Speranskaya[15].

The concentration of sulphuric acid used as the catalyst and the reaction temperature have a profound effect on the yield of the main products. The study of the effect of the concentration of the acid on the rate of reaction showed that the latter is proportional to the acid concentration[10]. However, in order to improve the selectivity of the process, it is preferable to use dilute acid solutions (up to 5 wt.%)[4,5]. The Prins reaction also takes place at room temperature, but useful rates of conversion of isobutene are attained only at 70–100°C.[16]

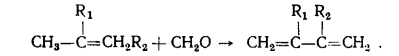
It has been stated in recent communications that, apart from sulphuric acid, cation-exchange resins can be used as catalysts in this reaction[2,17-20]. The application of Amberlite IR-120 and KU-2 resin (the latter produced in the USSR)[21] resulted in a 56% yield of dimethyldioxan with respect to the unreacted olefin. Ion-exchange resins as catalysts have a number of advantages, which are particularly important in the industrial application of the process.

Compared with isobutene, straight-chain butenes are much less reactive. In the condensation of a mixture of butenes, containing 20% of isobutene and 37% of straight-chain butenes, with formaldehyde during 5 h at 70°C, 70% of isobutene and only 3% of butenes reacted[17], but-2-ene reacting somewhat faster than but-1-ene[9,22]. In 3 h at 90°C 4-ethyl-1,3-dioxan was obtained from but-1-ene in 34% yield and a mixture of *cis*- and *trans*-isomers of 4,5-dimethyl-1,3-dioxan was obtained from but-2-ene in 74% yield. According to Farberov's data[4], straight-chain butenes are approximately equally reactive.

The condensation of pentenes with formaldehyde was investigated very recently using KU-2 cation exchanger as catalyst[23]. Substituted 1,3-dioxans are formed. The dioxan fraction (b.p. 152–154°C, yield 66.3%) isolated from the reaction products consisted of 4,4,5-trimethyl-1,3-dioxan and 5-ethyl-4-methyl-1,3-dioxan. t-Pentyl alcohol was also isolated from the products. The reactivities of the isomeric pentenes have been compared.

b. Condensation in the Presence of Heterogeneous Acid Catalysts at High Temperatures

This method has been described only in the patent literature[24-31]. It consists essentially in passing the olefin, aldehyde, and an inert diluent at 250–400°C over heterogeneous catalysts. Under these conditions, diene hydrocarbons are produced:



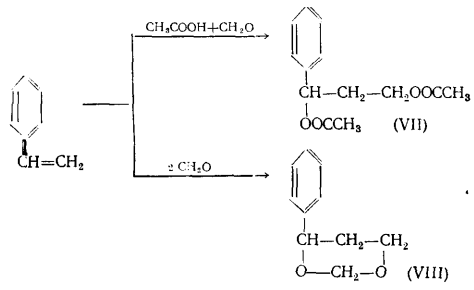
The best results were obtained when olefins with a tertiary carbon atom were used.

The reaction is carried out in the presence of a large excess of olefin (olefin : formaldehyde = 8 : 1), probably in order to suppress side-reactions, which lead to the formation of high-molecular-weight oxygen-containing products. In addition, the reaction products are diluted with a large volume of an inert diluent (nitrogen, carbon dioxide, lower saturated hydrocarbons) to suppress the polymerisation and condensation reactions. In this method the catalysts are mineral acids deposited on activated alumina, silica gel, magnesium oxide, or boron trioxide, synthetic catalysts for the cracking of petroleum, etc. The reactions take place at the normal or elevated (up to 7 atm) pressures. 4,4-Dimethyldioxan is also obtained in the condensation of isobutene with formaldehyde, using silica gel or aluminosilicates as catalysts at 500°C.[32] The acidity of the catalyst has a decisive effect on the yield of the main product in this case. Thus at $H_0 = 1.5-3.8$ (silica gel) a 97% yield of 4,4-dimethyldioxan was obtained.

2. SYNTHESIS OF 1,3-DIOXANS FROM ARYL-SUBSTITUTED OLEFINS

The literature dealing with the condensation of aryl-substituted and cyclic olefins was not reviewed by Arundale and Mikeska[1]. The condensation of styrene with formaldehyde in the presence of a mixture of sulphuric and glacial acetic acids was first investigated by Prins[33]. As a result of the condensation, he obtained the diacetate of

1-phenylpropane-1,3-diol and a certain amount of 4-phenyl-1,3-dioxan:

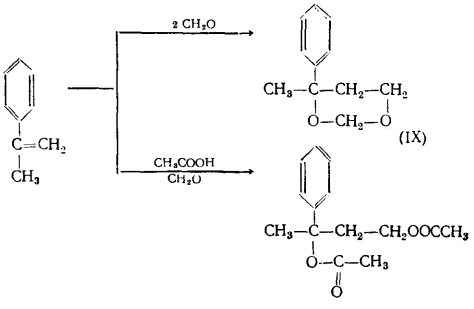


However, Prins erroneously regarded these compounds as derivatives of 2-phenylpropane-1,3-diol. Their true structure was established later[34].

It is noteworthy that, when the reaction is carried out in acetic acid solution, the yield of 4-phenyl-1,3-dioxan (VIII) is reduced due to the formation of the acetates of 1-phenylpropane-1,3-diol (VII). When 1,4-dioxan is used as the solvent, the yield of 4-phenyl-1,3-dioxan is increased to 78%.[35] With hydrochloric acid as the catalyst[36], the reaction can be carried out also in an inert hydrocarbon solvent. 4-Phenyldioxan was obtained in 88% yield by the condensation of styrene with a 37% solution of formaldehyde in the presence of sulphuric acid[35].

Backer[37] noted that the reaction of α-methylstyrene with formaldehyde in a mixture of 100% sulphuric and glacial acetic acids at 40°C is accompanied by extensive polymerisation of α-methylstyrene. Polymerisation can be partially suppressed if the reaction is performed at 0°C, but at this temperature the conversion of α-methylstyrene is low.

The reaction of α-methylstyrene with formaldehyde in the presence of a mixture of sulphuric and acetic acids has the following mechanism:



If orthophosphoric acid is used as the catalyst, the yield of 4-methyl-4-phenyl-1,3-dioxan (IX) can be increased to 75% with respect to the aldehyde.

4-Acetoxy-2-phenylbut-1-ene was obtained in 70% yield in the condensation of α-methylstyrene with formaldehyde in the presence of acetic acid[38]. Farberov[4] showed that the condensation of α-methylstyrene with formaldehyde is quite possible in the presence of 1–1.5% sulphuric acid. Here the yield of 4-methyl-4-phenyl-1,3-dioxan was 85%. In their study of the products of the reaction of anethole with formaldehyde by the NMR method, Smissman et al.[39] noted only the formation of the *cis*-isomers of 1,3-dioxan.

A detailed study of the condensation of α-methylstyrene with formaldehyde was made by French chemists[40], who used various methods for the identification of the chemical compounds (infrared spectroscopy, preparative chromatography, etc.) and isolated and described 15 compounds formed in this system. The reaction of α-methylstyrene with 37% aqueous solution of formaldehyde in the presence of KU-2 resin as the catalyst has been investigated[41].

3. SYNTHESIS OF 1,3-DIOXANS FROM HALOGENO-OLEFINS

Monohalogeno-olefins can react with formaldehyde to form halogeno-1,3-dioxans. 4-Chloromethyl-4-methyl-1,3-dioxan and 3-chloromethylbutane-1,3-diol are formed in the condensation of methylallyl chloride with paraformaldehyde in the presence of sulphuric acid or $BF_3.O(C_2H_5)_2$.[42]

Farberov and coworkers[43] investigated in detail the reaction of chloropropenes with paraformaldehyde under various conditions. The first attempts to prepare halogeno-substituted aryl-1,3-dioxans from halogenostyrenes proved unsuccessful. Beets and Drukker[44] failed in their attempt to condense α- and β-bromostyrenes with formaldehyde in the presence of 5% sulphuric acid. When 50% sulphuric acid was used, 4-aryl-5-halogeno-1,3-dioxans were obtained in 60–90% yield[45].

The work of Japanese and Italian chemists dealing with the condensation of β-bromostyrene and β-bromo-*p*-nitrostyrene with paraformaldehyde was published comparatively recently[46-48]. These studies are of great theoretical interest, since they led to the correction of certain aspects of the mechanism and stereochemistry of the Prins reaction. It is known that the electrophilic addition to carbon–carbon double bonds takes place in the *trans*-position, and this also holds for the Prins reaction.

It was shown in the above investigations that under certain conditions the Prins reaction is stereospecific, i.e. involves *cis*-addition. Thus *cis*-5-bromo-4-phenyl-1,3-dioxan was obtained in the condensation of *trans*-β-bromostyrene with paraformaldehyde.

While the condensation of monohalogeno-olefins with formaldehyde in the presence of dilute mineral acids leads to the formation of halogenated 1,3-dioxans, polyhalogeno-olefins give halogeno-substituted hydroxy-acids or alcohols, depending on the nature and concentration of the catalyst. Halogeno-substituted hydroxy-acids and their esters are obtained in the condensation of di-, tri-, and tetra-chloroethylene with formaldehyde in the presence of dilute sulphuric acid[49]. The condensation of the same olefins with paraformaldehyde in the presence of hydrochloric acid yields chloropropanols[50]. When paraformaldehyde is condensed with trichloroethylene in the presence of aluminium chloride as the catalyst, αβ-dichloropropionic acid, 2,3,3,3-tetrachloropropan-1-ol together, and di(2,3,3,3-tetrachloropropyl) ether are obtained[51].

4. SYNTHESIS OF 1,3-DIOXANS FROM CYCLIC OLEFINS

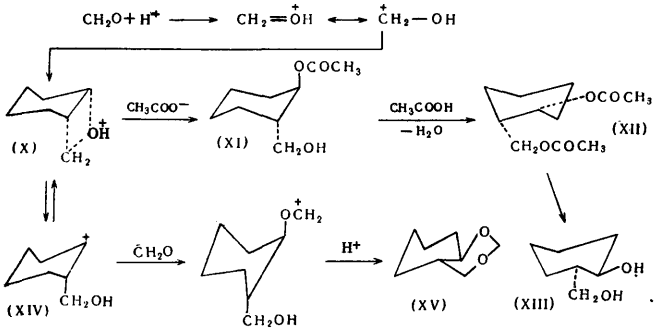
Arundale and Mikeska[52] were the first to show that in the presence of 45–55% sulphuric acid it is possible to condense cyclic olefins with formaldehyde to form 1,3-dioxans. When the reaction is carried out in the presence of sulphuric and acetic acids, the products include, together with 1,3-dioxans, a complex mixture, the main components of which are the diacetate of 2-hydroxymethylcyclohexanol, 3,4-tetramethylene-2,5-dihydrofuran, and 1-hydroxymethylcyclohexene[53-59].

Blomquist and Wolinsky[58] and Smissman and Mode[60] showed that the condensation of cyclohexene with formaldehyde in the presence of acid catalysts is a special case

of the electrophilic addition of an aldehyde to an olefin double bond[61-63]. The above workers noted that only the *trans*-isomers are formed in the reaction of cyclohexene with formaldehyde.

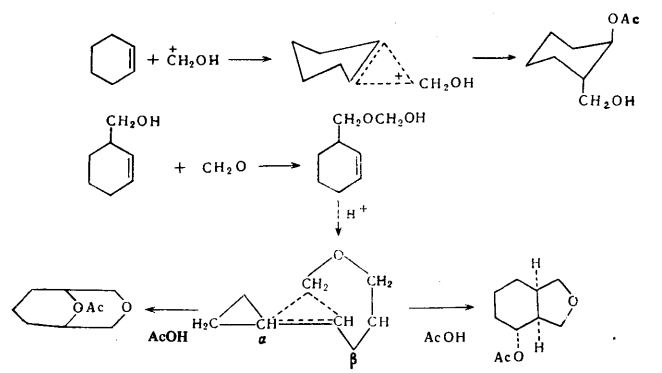
The high stereospecificity of the Prins reaction leads to the formation exclusively of *trans*-2-hydroxymethylcyclohexanol and also substituted 3-oxabicyclononanes in which the substituent in the hydrocarbon ring is in the *trans*-position relative to the heterocycle formed by *cis*-closure.

Blomquist and Wolinsky proposed a mechanism for the Prins reaction, which accounts for its stereoselectivity[58]. As a result of the protonation of formaldehyde and the attack by a solvated carbonium ion on the olefin double bond, a hybrid oxonium–carbonium ion, (X) ⇌ (XIV), is formed. The acetate ion attacks the oxonium–carbonium ion (X) from the least screened side, which leads to the formation, via a diaxial monoacetate stage (XI), of *trans*-diequatorial diacetate (XII), whose hydrolysis yields the diol (XI); the attack of formaldehyde on the carbonium ion (XIV) and subsequent cyclisation yield *trans*-1,3-dioxan (XV):



However, this mechanism does not explain the formation of side-products.

Dolby[59] proposed another mechanism for the Prins reaction. The intermediate product, which in Dolby's view controls the stereochemistry of the reaction, is a three-membered cyclic ion, analogous to the intermediate products suggested by other workers for electrophilic addition at the double bond:



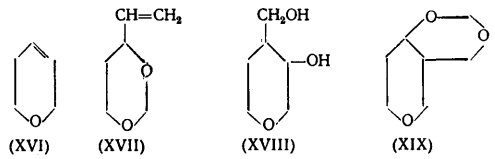
Smissman and coworkers studied the mechanism and the stereospecificity of the Prins reaction using the condensation of anethole with formaldehyde in the presence of an acid catalyst as an example[64,65].

The Prins reaction has been extended to the condensation of olefins not only with aldehydes but also with ketones. Fodor and coworkers[66] showed that 2-(α-hydroxyisopropyl)cyclohexanol forms (after hydrolysis) in the reaction of cyclohexene with acetone in the presence of sulphuric acid.

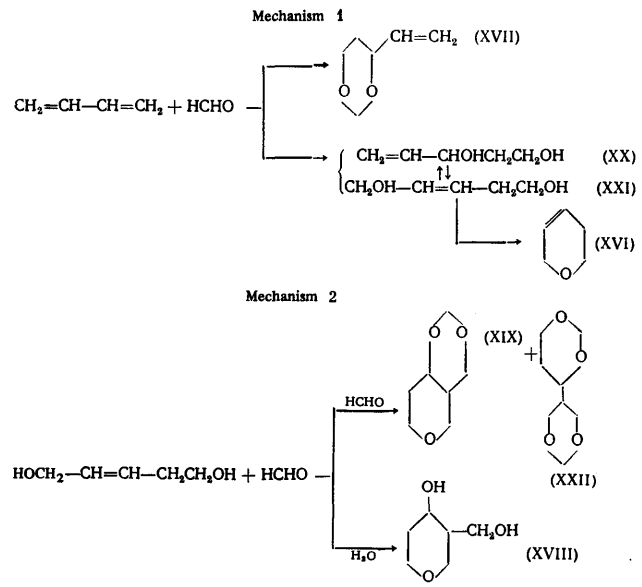
The condensation of cyclohexene and other cyclic olefins with formaldehyde in the presence of KU-2 cation-exchange resin has been investigated[67].

5. SYNTHESIS OF 1,3-DIOXANS FROM DIOLEFINS

A very small number of papers dealing with the condensation of diolefins with formaldehyde has been published. In 1955 Hanschke[68] showed that the condensation of butadiene with two moles of formaldehyde in the presence of sulphuric acid at 80°C yields a mixture of products, from which he isolated and identified 5,6-dihydro-2*H*-pyran (XVI), 4-vinyl-1,3-dioxan (XVII), tetrahydro-4*H*, 5*H*-pyrano[3,4-*d*]-1,3-dioxan (XIX), and the corresponding glycol (XVIII).



Extensive studies on the Prins reaction have been made in recent years at the French Petrochemical Institute. At the end of 1964 Hellin et al.[69] at this Institute published a paper describing the butadiene–formaldehyde system under the conditions of the Prins reaction. They studied the reaction at 80°C in aqueous sulphuric acid with the molar ratio formaldehyde : butadiene = 2; the duration of the reaction was varied from 30 min to 4 h. The authors quote the following two reaction mechanisms:

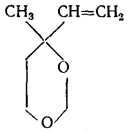


In mechanism 1 two isomers of pentenediol (XX) and (XXI) are formed as a result of 1,2- or 1,4-addition to butadiene. Of these isomers, the second, which has two primary hydroxyls and a double bond within the chain, [isomer (XXI)] is the more likely. Dihydro-5,6-α-pyran (XVI), which is one of the main products of the Prins reaction, forms on intramolecular conversion of pent-2-ene-1,5-diol (XXI) into an ether.

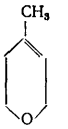
The multiplicity of the possible modes of the reaction leads to the formation of higher condensation products. In particular, diols with a double bond (see mechanism 2)

can react directly with formaldehyde to form large molecules—*trans*-trioxaperhydronaphthalene (XIX), dioxanyldioxan (XXII), and *trans*-hydroxyethyltetrahydropyranol (XVIII). The simultaneous presence of trioxaperhydronaphthalene and dioxanyldioxan confirms the above view rather than the possible occurrence in this case of the Prins reaction with 4-vinyl-1,3-dioxan.

The reaction with isoprene is even more complex[70]. The primary products are 4-methyl-4-vinyl-1,3-dioxan (XXIV) and 4-methyldihydro-5,6-pyran (XXV),

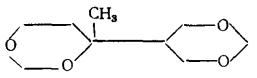


(XXIV)

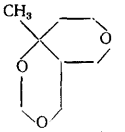


(XXV)

whose subsequent reactions lead to the appearance of more complex products: 5-(4′-methyl-1′,3′-dioxan-4′-yl)-1,3-dioxan (XXVI), *cis*- and *trans*-10-methyl-1,3,7-trioxaperhydronaphthalenes, and the corresponding diols:



(XXVI)



(XXVII)

In the USSR the reaction of diene hydrocarbons with formaldehyde in the presence of hydrochloric acid was investigated by Ustavshchikov and Fel'dblyum[71]. The reaction was studied mainly using butadiene (divinyl). The main reaction products were isolated and characterised. The reaction of the closest butadiene homologues, piperylene and isoprene, were studied in less detail. The reaction was carried out for 3–5 h at 20°C with the molar ratios diene : CH_2O : HCl = 1 : 1 : 2. It was established, on the basis of the rate of disappearance of formaldehyde, that piperylene and isoprene react approximately 1.5 times faster than divinyl.

In the reaction with divinyl the main products are 4-vinyl-1,3-dioxan, 3-chloromethyl-4-chlorotetrahydropyran, and the formals of the isomeric unsaturated chlorohydrins, for example 1-chloropent-2-en-5-ol. The cyclic formal of 3-hydroxymethyltetrahydropyran-4-ol was also isolated in small amounts.

In contrast to divinyl, piperylene and isoprene are mainly hydrochlorinated under the reaction conditions with formation of isomeric chloropentenes; 1,3-dioxans and the corresponding dichloro-derivatives of alkyl-tetrahydropyrans are also formed.

On the basis of their results, the authors proposed the following mechanism for the reaction between dienes and formaldehyde. Apparently the initial step is the protonation of the oxygen atom of formaldehyde:

$$\overset{+}{H} + O{=}CH_2 \rightleftarrows HO\overset{+}{C}H_2 .$$

The hydroxymethylcarbonium ions attack the diene molecules with formation of the carbonium ions A and B,

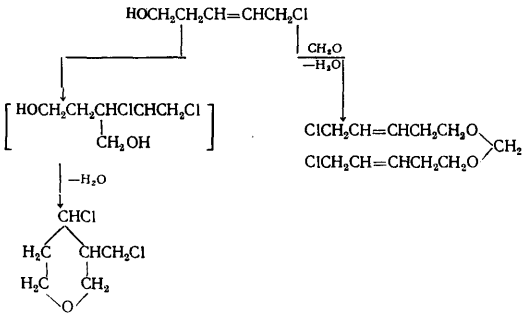
$$CH_2{=}CH{-}CH{=}CH_2 + \overset{+}{C}H_2OH \longrightarrow \begin{cases} \overset{+}{C}H_2{-}CH{=}CH{-}CH_2CH_2OH & (A) \\ CH_2{=}CH{-}\overset{+}{C}H{-}CH_2CH_2OH . & (B) \end{cases}$$

whose reaction with formaldehyde or a chloride ion leads to the formation of 1,3-dioxan or chlorohydrin respectively:

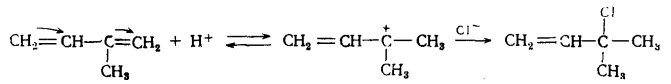
$$\overset{+}{C}H_2{-}CH{=}CH{-}CH_2CH_2OH \xrightarrow{Cl^-} ClCH_2{-}CH{=}CH{-}CH_2CH_2OH$$

$$CH_2{=}CH{-}\overset{+}{C}HCH_2CH_2OH \xrightarrow[-H^+]{CH_2O} CH_2{=}CH{-}\underset{\displaystyle O{-}CH_2{-}O}{\underset{|}{CH}}{-}CH_2{-}CH_2$$

Dioxan has actually been isolated as one of the reaction products. The chlorohydrin probably undergoes secondary reactions by the mechanism



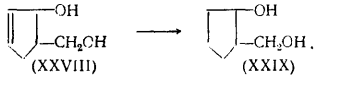
When the diene is isoprene or piperylene, the protons can also react directly with the latter, which leads to the formation of carbonium ions derived from hydrocarbons and the final products are chloropentenes:



However, the mechanism of the formation of the other products is the same.

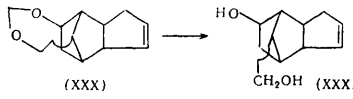
Beets and Drukker[44] investigated the reaction of cyclopentadiene with formaldehyde. When the reaction was carried out in an autoclave at 185°C without catalysts, only a resinous product was obtained. When cyclopentadiene was treated with an excess of 36% aqueous solution of formaldehyde in the presence of sulphuric acid, the authors obtained 2-hydroxymethylcyclopent-4-enol (XXVIII) in 20% yield and the corresponding dioxan. The cyclopentadiene reacted completely; also present were high-boiling products, from which the pure components could not be isolated. When the amount of formaldehyde per mole of diene was reduced from 2.72 to 1.23 moles, the yield of the corresponding dioxan fell and the amount of hydroxylated high-boiling products increased.

2-Hydroxymethylcyclopent-4-enol (XXVIII) was also obtained on heating cyclopentadiene in acetic acid solution with formaldehyde in the presence of catalytic amounts of toluenesulphonic acid. Its structure was demonstrated by conversion into the saturated diol (XXIX) by catalytic hydrogenation:



(XXVIII) (XXIX)

Zimmermann and Reiners described the Prins reaction with dicyclopentadiene[73]. They carried out the reaction in formaldehyde solution in the presence of sulphuric acid at 80°C. The dioxan (XXX) probably forms under the reaction conditions. The diol (XXXI) was obtained by the reaction of the same compound with an excess of methyl alcohol and a small amount of sulphuric acid:



(XXX) (XXXI).

6. SYNTHESIS OF 1,3-DIOXANS FROM ENYNE AND DIENYNE HYDROCARBONS

The first studies on the condensation of enyne and dienyne hydrocarbons with formaldehyde in the presence of sulphuric acid were made by Matsoyan and Saakyan[74]. It was established that formaldehyde reacts selectively with dienes, the reaction involving exclusively the substituted double bond of the divinylacetylene hydrocarbon. During the condensation substituted 1,3-glycols are formed in small amounts as side-products, but they are difficult to purify.

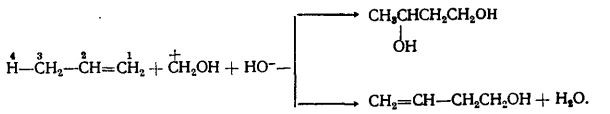
The reaction of formaldehyde with tertiary vinylacetylene alcohols was carried out using KU-1 and KU-2 cation-exchange resins as the catalysts[75]. It was shown that in this case the main products are 1,3-dioxans and a small amount of 1,3-glycols of the vinylacetylene series. The authors of the present review made a detailed study of the optimum conditions for the condensation of ethynyldimethylvinylmethanol with formaldehyde in the presence of KU-2 cation-exchange resin[76].

7. THE MECHANISM OF THE PRINS REACTION

Franzen and Krauch[77] believe that the initial step in the reaction is the addition of a proton to the oxygen atom of the carbonyl group with formation of the carbonium ion $R-\overset{+}{C}-OH$, which then attacks the double bond at the site of the highest electron density. The new carbonium ion can react further in three ways. In the interaction with an excess of the aldehyde, dioxan is produced, the reaction with water leads to the formation of a glycol, and, finally, the removal of a proton results in the formation of an unsaturated alcohol. The glycol and dioxan are formed independently of one another; although the glycol can, in fact, be produced from 1,3-dioxan, under the reaction conditions this happens rarely.

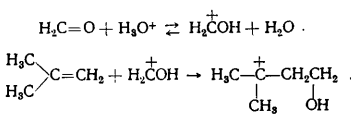
The third reaction, i.e. the removal of a proton, is observed only in the addition of formaldehyde. A proton is removed (in accordance with the Hofmann rule) from the carbon atom adjacent to the carbonium centre which has the smallest number of substituents. The removal of a proton from the CH_3 group can be facilitated by the presence of a hydroxyl. The formation of the glycol greatly depends on the basicity of the medium, since at high pH values the 1,3-glycol decomposes into an olefin and an aldehyde.

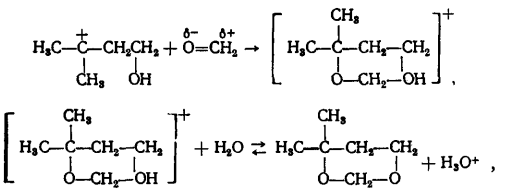
According to Farberov's hypotheses[4,5], the diol results from the reaction at 1,2-bonds and the unsaturated alcohol from the reaction at 1,4-bonds:



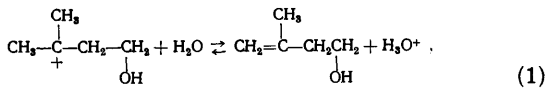
Generalising the results obtained, the following general mechanism of the Prins reaction can be put forward[20,78], for isobutene and formaldehyde as examples:

a. main reaction:

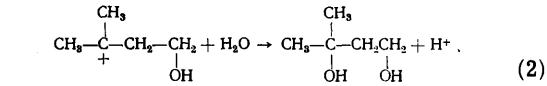




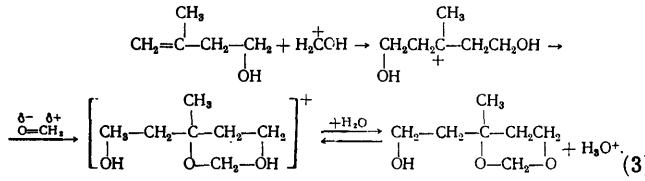
b. side-reactions:



(1)

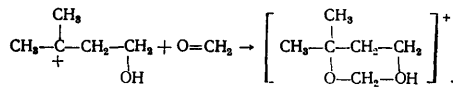


(2)



(3)

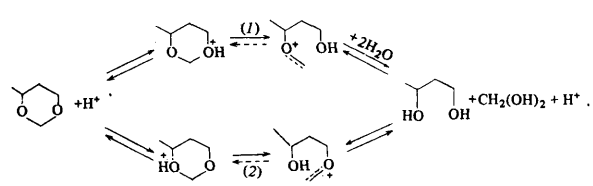
Kinetic studies show that the reaction on ion-exchange resins is of third order, and the rate-limiting stage is the reaction of the secondary carbonium ion with the aldehyde[20]



8. PROPERTIES AND APPLICATIONS OF 1,3-DIOXANS

1,3-Dioxans are widely used as the starting materials for the synthesis of varnishes[79], resins[80], detergents[81], antibiotics[46,47], and insecticides[82]. In practice the most important are the syntheses of diene hydrocarbons based on them. Since hydrolysis is an intermediate stage of the conversion of alkyldioxans into dienes, a number of papers dealing with this problem has appeared in recent years in the scientific literature. In the hydrolysis (methanolysis) of alkyl-1,3-dioxans in the presence of small amounts of sulphuric acid and an excess of methyl alcohol, it proved possible to isolate diols in yields of up to 80%.[83] However, the hydrolysis of alkyldioxans in which the oxygen atom is linked to a tertiary carbon atom is much more difficult. The yield of the diol is at best not more than 50%. Using a cation exchanger instead of sulphuric acid in the methanolysis of 4-methyl-1,3-dioxan, the diol was obtained in quantitative yield[84].

The kinetics of the hydrolysis of a number of substituted 1,3-dioxans in water and aqueous dioxan have been investigated at 60–70°C.[85-87] The hydrolysis of 1,3-dioxans can take place in two ways:



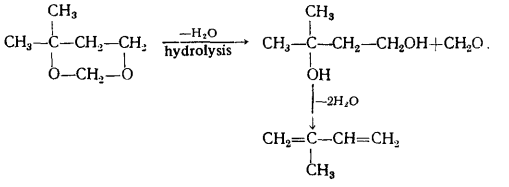
Kinetic measurements show that the first mode of reaction is the more likely.

Dehydration of glycols leads to the formation of the corresponding diene hydrocarbons, but since the yield of glycols is low because of hydrolysis, this method is unsuitable for the industrial manufacture of diene hydrocarbons. Therefore another procedure was chosen, which permits the synthesis of diene directly in one stage—the catalytic dissociation of alkyldioxans in the presence of suitable catalysts. The choice of the catalyst capable of selective dissociation of the alkyldioxan with a high activity was difficult because reactions of this kind had not been investigated in chemical engineering.

The patent literature describes methods of synthesising dienes on the basis of dioxans[1], but in the scientific literature this process had not been elucidated until the publication of the work of Farberov and coworkers[88]. In the course of their studies over a number of years on the synthesis of isoprene from isobutene and formaldehyde, they investigated in detail the catalytic dissociation of 4,4-dimethyl-1,3-dioxan to isoprene in the gas phase over a solid catalyst.

Best results were obtained when Group II metal phosphates were used as catalysts, in particular calcium phosphates. These catalysts are very active and selective, exhibit high productivity, and are fairly stable. An essential condition is that the process be carried out in the presence of water vapour, which is probably connected with the dehydration of acid calcium phosphates.

Bearing in mind that an increase in the concentration of water vapour in the reaction mixture results in an acceleration of the catalytic dissociation of dimethyldioxan, Farberov proposed a mechanism, according to which water participates directly in the reaction. As a result of the reaction with water, dimethyldioxan is hydrolysed on the catalytic surface to the diol, which is then dehydrated to give isoprene:



As a result of a detailed study of the conditions of the catalytic dissociation of dimethyldioxan [at 375°C, 1:14 (molar ratio) dilution with water vapour, volume flow rate of dimethyldioxan 0.7 ml per ml of catalyst per hour] isoprene yields of 75–85% with respect to the dioxan passed through and 80–85% with respect to the dioxan decomposed were attained. The method thus developed served as the basis of the industrial manufacture of isoprene of a high degree of purity.

9. INFRARED SPECTRA OF SUBSTITUTED 1,3-DIOXANS

The available data on the infrared spectra of 1,3-dioxans reveal a very complex structure of the bands, the number of characteristic bands being variable[21,89,90]. 1,3-Dioxans substituted in position 4 constitute a system characterised by four bands[85]: two very intense bands in the region 1166 ± 20 cm^{-1} and 1037 ± 15 cm^{-1} and two other less intense bands in the region 1090 ± 25 cm^{-1} and 985 ± 10 cm^{-1}.

10. SYNTHESIS OF 1,3-DIOXANS FROM TERPENE HYDROCARBONS

Until recently the behaviour of the extensive class of terpene hydrocarbons in the Prins reaction was virtually uninvestigated, although the possibility of the condensation of aldehydes with olefins was first demonstrated by Prins for α-pinene and camphene as examples[91]. However, Prins did not investigate these reactions in detail and merely indicated the physicochemical characteristics of some of the condensation products (without stating the yield). Serious studies on the condensation of α-pinene, camphene, dipentene, and β-pinene were begun by Japanese chemists. Watanabe, who studied the condensation of formaldehyde with α-pinene in a mixture of acetic and phosphoric acids and acetic anhydride, obtained a mixture of the acetates of α-terpineol, (±)-isoborneol, and 6-acetoxymethyl-$\Delta^{1,8(9)}$-*p*-pentadiene, whose structure was demonstrated by its further conversion into (±)-carbomenthone[92].

On the other hand, when a mixture of α-pinene, formaldehyde, and 60% perchloric acid was stirred for 6 h at 95–100°C, 1-methyl-4-(4′-methyl-1′, 3′-dioxacyclohex-4′-yl)cyclohexene (I) and bisdioxan $C_{14}H_{24}O_4$ (II) were obtained. The structure of the products (I) and (II) was confirmed by hydrogenation[92].

Using various catalysts (98% sulphuric acid, 85% phosphoric acid, 60% perchloric acid), Watanabe and coworkers isolated a mixture of 8-hydroxymethylcamphene and spiro-[2,2-dimethylnorbornane-3,1′-(2′, 4′-dioxacyclohexane)], with an overall yield of 56.3%, in the condensation of camphene with formaldehyde[93].

A complex mixture of products was also obtained in the condensation of dipentene with formaldehyde in the presence of perchloric acid. Apart from the initial products, a fraction boiling at 104–109°C at 7 mmHg was isolated from the reaction mixture freed from impurities by steam distillation. After chromatography on silica, a product was isolated and identified by infrared spectroscopy as a mixture of 1-methyl-4-(4′-methyl-1′, 3′-dioxacyclohex-4′-yl)cyclohexene and 8-isopropyl-1-methyl-2,4-dioxabicyclo[4,4,0]decane, which the authors regard as the primary products of the reaction between dipentene and formaldehyde[94,95]. A complex mixture of products also resulted in the condensation of limonene with paraldehyde in the presence of zinc chloride[96].

The authors of the present review investigated the condensation of α-pinene, dipentene, and camphene with formaldehyde in the presence of KU-2 cation-exchange resin[97].

While the present review was with the editors, a number of communications by the authors of the review dealing with the Prins reaction in the presence of KU-2 cation-exchange resin was published[98–101].

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Electrical and Photoelectric Properties of Organic Polymeric Semiconductors

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I. INTRODUCTION

Organic compounds containing systems of conjugated multiple bonds are now termed organic semiconductors: the conductivity of these substances is electronic, increases exponentially with temperature, and is greater (as a rule) than the conductivity of normal organic compounds.

During the past 10 years, in addition to extensive studies of the semiconducting properties of low-molecular-weight organic compounds, we have witnessed a significant volume of work on the synthesis and characterisation of a new class of organic semiconductors: the macromolecular compounds. The rising interest in semiconducting polymers is due, on the one hand, to recent advances in the physics and technology of inorganic semiconductors, which have led to a search for new materials showing semiconductor properties, and on the other hand to the successful preparation of polymers with a wide variety of physicochemical properties, resulting in widespread applications of polymers in technology. The attractive prospect of developing simple models, leading to a deeper understanding of some biophysical processes (which take place, as a rule, in complex macromolecular systems) has undoubtedly been an additional stimulus to developments in the physics of electronic phenomena in organic systems.

The present review deals with the most important experimental and theoretical data relating to organic semiconducting polymers having an electronic (as distinct from an ionic) conduction mechanism. Since studies on low-molecular semiconductors have led the way to an understanding of the semiconductivity of polymers, we shall briefly review the basic ideas of organic low-molecular semiconductor physics without attempting to cover the literature in detail. The later sections will discuss, separately, the electrical properties of organic semiconducting polymers and photoelectric processes in these materials.

We thought it desirable to devote a whole section to the photoelectronics of organic polymers because the subject is of very recent origin (5 years at the most), and has not so far been reviewed in any way. The aim of this review is to familiarise the reader with the physical aspects of organic polymeric semiconductors.

II. LOW-MOLECULAR-WEIGHT ORGANIC SEMICONDUCTORS

The following basic laws have been shown to apply[1-8] to low-molecular-weight organic semiconductors (dyestuffs, aromatic hydrocarbons):

1. The dark conductivity (σ_d) varies with temperature (T) according to the law

$$\sigma_d = \sigma_0 \exp(-E_d/2kT)\dagger \qquad (1)$$

where σ_0 is a constant for the particular semiconductor, k is Boltzmann's constant, and E_d is the thermal activation energy for dark conduction. E_d usually varies between 0.5 and 3 eV, and the value of σ_d at room temperature can vary between wide limits (10^{-1}–10^{-20} ohm^{-1} cm^{-1}). The thermal activation energy for dark conduction corresponds to the energy of the long-wave edge of the optical absorption curve, and decreases with increasing number of π-electrons in the molecule.

† The form of the exponent depends on the conduction mechanism assumed.