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ADDITION OF α-CHLOROALKYL ETHERS TO UNSATURATED COMPOUNDS

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1. INTRODUCTION

In his review of the addition of alkyl halides to olefins Arbuzov[1] dealt in some detail with the El'tekov[2] and Kondakov[3,4] reaction, and Summers[5] reviewed the preparation and reactions of α-chloro-ethers, covering the literature up to 1955; however, in neither review did the addition of α-chloro-ethers to unsaturated compounds receive much attention. Nevertheless, in recent years much interesting work on the electrophilic addition of chloro-ethers to multiple bonds has appeared. In the present paper we have attempted to collect and classify the considerable material which has now accumulated on this subject.

2. ADDITION OF α-CHLOROALKYL ETHERS TO OLEFINS

α-Chloroalkyl ethers are much more reactive than alkyl halides, and they behave analogously to hydrogen halides. Cocker et al.[6] associate the activity of the labile chlorine atom in α-chloro-ethers with the simultaneous existence of a carbonium ion and an oxonium ion:

$$R-\overset{+}{C}H-\ddot{O}-R' \longleftrightarrow R-CH=\overset{+}{\ddot{O}}-R'.$$

Chloromethyl ether undergoes rapid hydrolysis and alcoholysis in aqueous and alcoholic solutions, yielding formaldehyde and a dialkoxymethane respectively. The rapidity of such processes has led many workers to conclude that the reactions are unimolecular, and this has been confirmed kinetically[7]. The rate-determining step is ionisation of the chloro-ether to produce a mesomeric carbonium ion, which rapidly adds on a hydroxide or alkoxide ion from the solvent:

$$CH_3-\ddot{O}-CH_2-Cl \xrightarrow[\text{slow}]{} CH_3-O-\overset{+}{C}H_2 + Cl^-,$$

$$ROH + CH_3O-\overset{+}{C}H_2 \xrightarrow[\text{fast}]{} CH_3OCH_2OR + H^+$$

(R = H or alkyl).

At room temperature in anhydrous solvents (or in the absence of a solvent), α-chloroalkyl ethers add to olefins in the presence of acidic catalysts by an ionic mechanism

in almost every case[8]. Various catalysts may be used, e.g. bismuth trichloride[9,10], mercuric chloride[11], or, most frequently, zinc chloride[9,11].

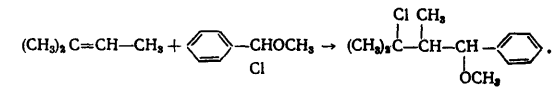
Scott in 1935 was the first to show[12] that chloromethyl ethers add to propene in the presence of bismuth trichloride to form 3-chloro-1-methoxybutane; the addition follows the Markovnikov rule:

$$CH_3{-}CH{=}CH_2 + CH_3OCH_2Cl \xrightarrow{BiCl_3} CH_3CHCl{-}CH_2CH_2OCH_3.$$

Straus and Thiel[11] investigated the addition of chloromethyl ethers to isobutene in the presence of mercuric chloride, and obtained the corresponding chloro-ethers (I):

$$(CH_3)_2C{=}CH_2 + ROCH_2Cl \xrightarrow{HgCl_2} (CH_3)_2CCl{-}CH_2CH_2OR. \qquad (I)$$

They also found that the α-chlorobenzyl ether can add to olefins under these conditions[11]:

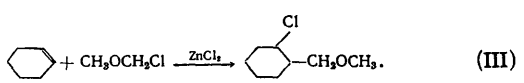


Mamedov, Zeinalov, and Pishnamez-zade[13-15] developed a simple method for the preparation of γ-halogeno-ethers (II) by addition of various chloro- or bromo-methyl ethers to olefins in the presence of zinc chloride:

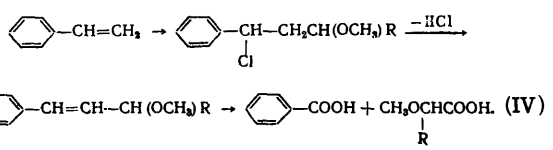
$$R{-}CH{=}CH{-}R' + R''OCH_2X \rightarrow \underset{X}{\overset{}{RCH}}{-}\underset{R'}{\overset{}{CH}}{-}CH_2OR''. \qquad (II)$$

The product yield is lower with ethylene than with its homologues. Certain of the resulting γ-halogeno-ethers possess acaricidal and insecticidal properties[16].

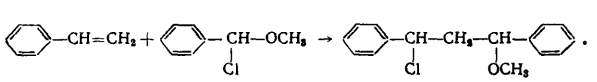
Chloromethyl ethers also add to cycloalkenes in the presence of zinc chloride. Straus[11] and Nenitzescu[17] obtained 1-chloro-2-methoxymethylcyclohexane (III) from cyclohexene and chloromethyl ether:



α-Chloroalkyl ethers add to styrene to form the corresponding chloro-ether[18,19]; the structure of the product (IV) is proved by the removal of hydrogen chloride and subsequent oxidation of the unsaturated ether[19]:



α-Chlorobenzyl ether also adds to styrene[11]:



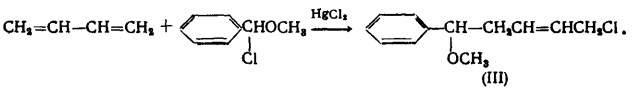
3. ADDITION OF α-CHLOROALKYL ETHERS TO CONJUGATED DIOLEFINS

The addition of chloromethyl ethers to butadiene was accomplished in 1935–1936 by Scott[12] and Straus[11] in the presence of mercuric chloride or zinc chloride, giving a mixture of two isomeric chlorides, the 1,2-addition product 3-chloro-5-methoxypent-1-ene (I) and the 1,4-addition product 1-chloro-5-methoxypent-2-ene (II):

$$CH_2{=}CH{-}CH{=}CH_2 + CH_3OCH_2Cl \xrightarrow{ZnCl_2} \underset{(I)}{CH_3OCH_2CH_2CHCl{-}CH{=}CH_2} \quad \underset{(II)}{CH_3OCH_2CH_2CH{=}CHCH_2Cl}.$$

When distilled under normal conditions the 1,2-addition product isomerised completely into the 1,4-addition product.

In the reaction of α-chlorobenzyl methyl ether with butadiene the only product is that of 1,4-addition (III):[11]



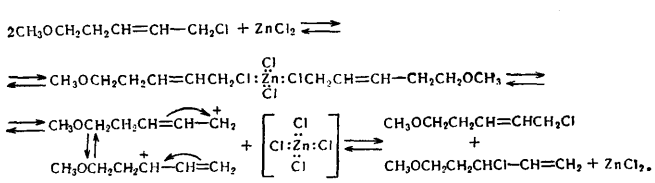
Pudovik, Arbuzov, and coworkers[20,21] investigated the addition of chloromethyl ethers to butadiene in some detail, and studied the resulting alkoxyalkyl chlorides; similar results were also obtained by other workers[22]. The total yield is 75%, comprising 75–80% of 1,2-addition product and 25–20% of 1,4-addition product. Under the influence of the zinc chloride catalyst there is mutual isomerisation of the alkoxyalkyl chlorides, so that a mixture is obtained containing 55% of the 1,4-addition product and 45% of the 1,2-addition product:

$$ROCH_2CH_2CH_2CHCl{-}CH{=}CH_2 \xrightarrow{ZnCl_2} ROCH_2CH_2CH{=}CHCH_2Cl.$$

In the absence of catalyst, both isomers remain unchanged for at least one year: i.e. they do not isomerise[20].

The action of 10% zinc chloride causes 90–93% isomerisation of the 1,2-addition product to the 1,4-addition product, the reverse process occurring only to the extent of 4–7%.[20] Pudovik and Arbuzov also show that in the absence of catalysts the alkoxyalkyl chlorides do not isomerise at 100°, while at 140° the 1,2-addition product is quantitatively isomerised into the 1,4-addition product.

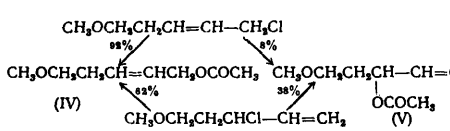
In the presence of zinc chloride the mutual isomerisation of the two isomeric chlorides is represented as follows[20]:



Meisenheimer and Schmidt[23] show that the allylic rearrangement can also occur under the influence of various chance factors (composition of the glass, contamination).

From the above, it may be said that chloromethyl ethers add to butadiene almost exclusively in the 1,2-position, but since the 1,2-addition products are very readily isomerised into the 1,4-addition products under the experimental conditions, the 1,4-isomer predominates in the final reaction product.

Allylic rearrangements occur not only with the products of the addition of chloromethyl ethers to butadiene, but also in the preparation of their derivatives. For example, with sodium acetate 1-chloro-5-methoxypent-2-ene gives the normal substitution product (IV) in 92% yield and the isomeric product (V) in 8% yield, while 3-chloro-5-methoxypent-1-ene gives 62% of the isomeric product (IV) and only 38% of the normal product (V):[24]

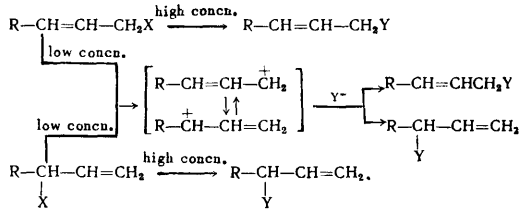


Both isomeric chlorides react analogously with sodiomalonic ester[25], phenylmagnesium bromide[26], and ammonium thiocyanate[22], but with alcohols in the presence of potassium hydroxide 1-chloro-5-methoxypent-2-ene gives the corresponding normal product, a 1,5-dialkoxypent-2-ene, in almost quantitative yield[8].

There have been many examples of the production of two isomers, depending on the reaction conditions, in the nucleophilic substitution of the chlorine in allyl chlorides, and various explanations for this have been proposed[27-33]. Prevost[30] considers it to be the result of ionisation of the rearranging molecule to produce the corresponding carbonium ion:

$$R{-}CH{=}CH{-}CH_2Cl \rightarrow R{-}\overset{+\delta}{C}H{-}CH{-}\overset{+\delta}{C}H_2.$$

It has been shown that nucleophilic substitution in allenic systems can take place by either a unimolecular or a bimolecular mechanism[34]: if the attacking reagent is added in small portions, the reaction proceeds by a unimolecular mechanism, either of the isomeric chlorides producing a mixture of the isomeric products corresponding to the two isomeric carbonium ions; while if the attacking reagent is added in high concentrations, it is mainly the normal reaction products which are formed:

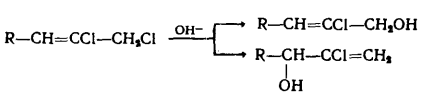


However, allylic systems do exist where no rearrangement occurs. For example, no isomeric products are obtained when the primary chlorine atom of 5-alkoxy-1,3-dichloroalk-2-enes (VI) is hydrolysed to give the corresponding alcohols or react to produce ethers, amines, etc.[35,36]:

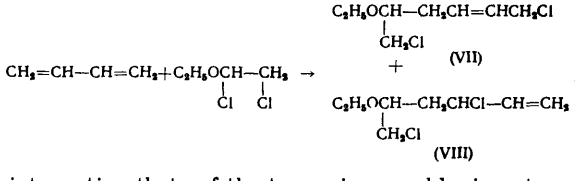
$$ROCH_2CH_2CCl{=}CH{-}CH_2Cl \xrightarrow{Y^-} ROCH_2CH_2CCl{=}CHCH_2Y.$$
(VI)

Y=OH, N<; OR'

Some allylic rearrangement occurs in the hydrolysis of 1,2-dichloroalk-2-enes, the isomeric chloro-alcohols being obtained in addition to the normal products[37]:

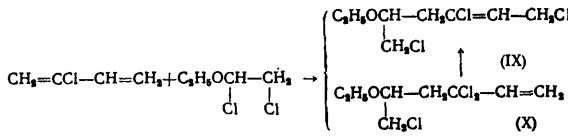


Pudovik[38] was the first to treat 1,2-dichlorodiethyl ether with butadiene in the presence of zinc chloride, obtaining 74% of the 1,4-addition product (VII) and 26% of the 1,2-addition product (VIII):



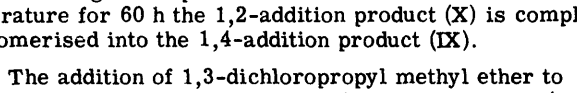
It is interesting that, of the two primary chlorine atoms in the 1,4-addition product (VII), only the α-chlorine atom can react further, the γ-chlorine atom being unreactive[38].

In the presence of zinc chloride 1,2-dichlorodiethyl ether also adds to chloroprene by 1,4- and 1,2-addition, forming 1,3,6-trichloro-5-ethoxyhex-2-ene (IX) and 3,3,6-trichloro-5-ethoxyhex-1-ene (X):[39]

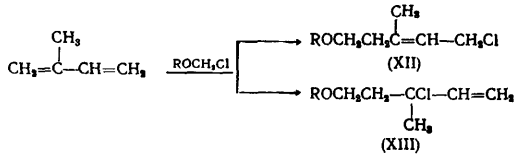


On standing in the presence of zinc chloride at room temperature for 60 h the 1,2-addition product (X) is completely isomerised into the 1,4-addition product (IX).

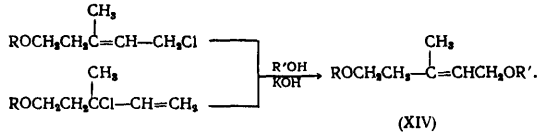
The addition of 1,3-dichloropropyl methyl ether to chloroprene produces only the 1,4-addition product (XI):[40]



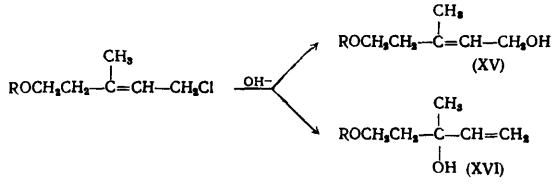
Chloromethyl ethers add to isoprene analogously to the above reactions, but the yield does not exceed 30–37%, and in the reaction products (XII) and (XIII) the 1,4-addition product (XII) predominates[41]. The mutual isomerisation of these two isomers is very rapid[41], and the equilibrium concentration of the 1,4-addition product (XII) is 90–92%



In the presence of potassium hydroxide the two isomers give the same product (XIV) with alcohols[41]:



Hydrolysis of 5-alkoxy-1-chloro-3-methylpent-2-enes (XII) with 15% aqueous potassium carbonate gives the two isomeric alkoxy-alcohols (XV) and (XVI):[42]



The addition of chloromethyl ethers to chloroprene in the presence of zinc chloride has been studied in some detail; the only product is that of 1,4-addition, the 5-alkoxy-1,3-dichloropent-2-ene (XVII):[35,43]:

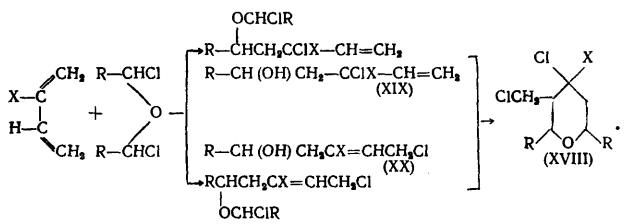
$$CH_2{=}CCl{-}CH{=}CH_2{+}ROCH_2Cl \xrightarrow{ZnCl_2} ROCH_2CH_2CCl{=}CHCH_2Cl.$$
(XVII)

These dichlorides are very reactive, and the primary chlorine atom takes part in all the reactions typical of alkyl halides[44-48].

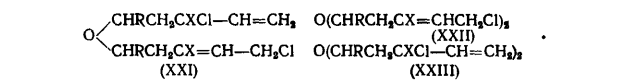
α-Chloroalkyl ethers add to isoprene, chloroprene, and butadiene in the presence of zinc chloride in an analogous manner[40,49]:

$$CH_2{=}\underset{X}{C}{-}CH{=}CH_2{+}ROCHCl \rightarrow ROCH\underset{R'}{C}H_2C{=}CH\underset{R'}{C}H_2Cl.$$
(X=H; CH_3; Cl)

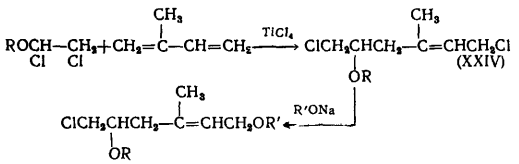
The addition of bis-α-chloroalkyl ethers to chloroprene and isoprene in the presence of zinc chloride produces mainly the tetrahydropyran derivatives (XVIII):[50]



There are also obtained small amounts of chloro-alcohols (XIX) and (XX) produced by hydrolysis of the intermediate ethers, and products of the addition of the bis-α-chloroalkyl ethers to two molecules of the diene (XXI)–(XXIII):[54]

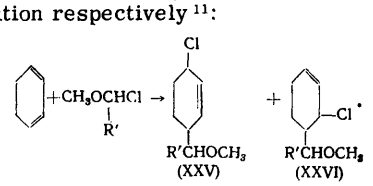


In the production of the vitamin A side-chain, a 1,2-dichloroethyl ether was added to isoprene in the presence of titanium chloride, to give the 1,4-addition product (XXIV),[51] only one primary chlorine atom of which undergoes further reaction:

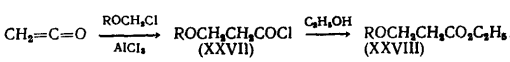


(R′ = CH_3CO or Alk).

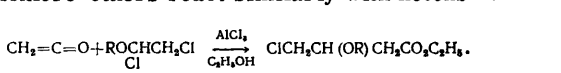
Chloromethyl ethers add analogously to cyclic conjugated dienes, e.g. cyclohexadiene, giving the two isomeric chlorides (XXV) and (XXVI), which are the products of 1,4- and 1,2-addition respectively[11]:



Chloromethyl ethers add to ketens in the presence of aluminium chloride. However, the expected alkoxylated acid chlorides (XXVII) have not been isolated, but have been treated with alcohol to give ethyl β-alkoxypropionates (XXVIII):[52]

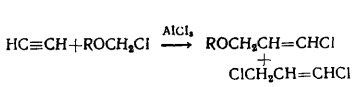


$\alpha\beta$-Dichloro-ethers react similarly with ketens[53]:



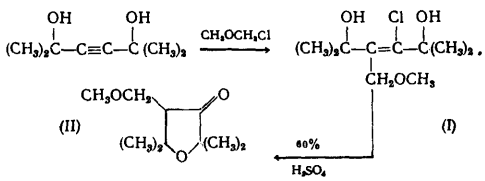
4. ADDITION OF α-CHLOROALKYL ETHERS TO ACETYLENIC, VINYLACETYLENIC, AND DIVINYLACETYLENIC SYSTEMS

Chloromethyl ethers add to acetylene in the presence of aluminium chloride to give mainly 3-alkoxy-1-chloroprop--1-ene but with some 1,3-dichloroprop-1-ene[54]:



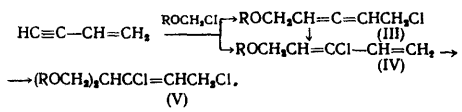
Phenoxymethyl chloride does not add to acetylene under these conditions[54].

Chloromethyl ethers add to the triple bond of tetramethylbutynediol in the presence of aluminium, tin, or zinc chloride to produce the corresponding chlorovinyl glycol (I), which when treated with 60% sulphuric acid forms tetrahydro-4-methoxymethyl-2,2,5,5-tetramethyl--3-oxofuran (II):[55]



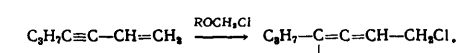
The addition of chloromethyl ethers to butyne-1,4-diols and their mono- and di-ethers proceeds analogously[55].

The addition of chloromethyl ethers to vinylacetylenic compounds has also been investigated. Dykstra[10] was the first to show that in the presence of bismuth trichloride they add to butenyne itself in the 1- and 4-positions. The product (III) can isomerise under the experimental conditions, or in the presence of cuprous chloride in 18% hydrochloric acid, and the resulting alkoxy-chloride (IV) can add a further molecule of chloromethyl ether under the given conditions, to form the dichloride (V):[56]

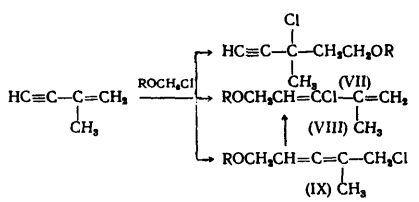


Zinc chloride produces the same reactions[56,57]. Dykstra prepared these chlorides in order to investigate their polymerisation, but the polymers obtained were not considered to be of good quality.

Under the conditions given above, chloromethyl ethers add to hept-1-en-3-yne to produce only the 1,4-addition product (VI), the isomeric chloride not being obtained. The product (VI) does not isomerise either under the experimental conditions or under the influence of cuprous chloride in 18% or 36% hydrochloric acid[56]:

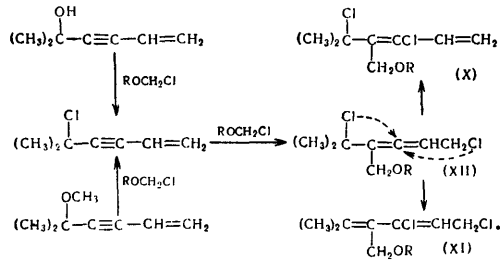


With 2-methylbut-1-en-3-yne, however, addition under the above conditions produces the three difficultly separable alkoxy-chlorides (VII)–(IX):[58]



The addition of chloromethyl ethers to 2-methylhex-5--en-3-yn-2-ol, to its methyl ether[59], or to 5-chloro-5--methylhex-1-en-3-yne[60] produces, in all cases, the same mixture of the two isomeric dichlorides (X) and (XI). Apparently the alkoxy- or hydroxy-group is first replaced by chlorine from the chloromethyl ether to give the corresponding chloro-compound, and the latter then undergoes

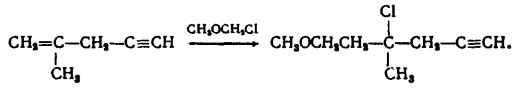
1,4-addition to the chloromethyl ether (as it does to hydrogen chloride[61]) to form the intermediate allenic dichloride (XII), which under the experimental conditions isomerises to produce a mixture of the two dichlorides (X) and (XI):



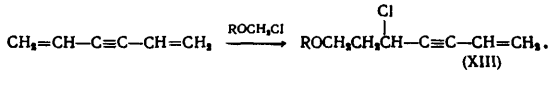
Unlike the ethers of dimethyl(vinylethynyl)carbinol [2-methylhex-5-en-3-yn-2-ol], those of primary and secondary vinylethynylcarbinols add chloromethyl ethers normally, i.e. by 1,4-addition, producing an allenic chloride which is not isomerised under the experimental conditions or under the influence of cuprous chloride in 18% or 36% hydrochloric acid[59]:



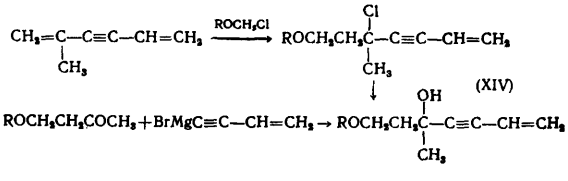
The addition of chloromethyl ethers to allylacetylenes [pent-1-en-4-ynes] has not been investigated; there is only one patent, describing the addition to 2-methylpent-1-en-4-yne, which takes place at the double bond according to Markovnikov's rule[62]:



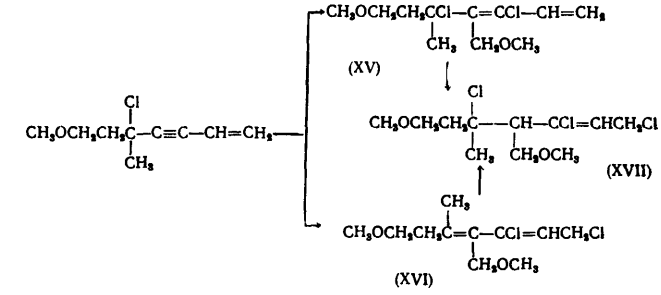
In the presence of zinc chloride chloromethyl ethers add to hexa-1,5-dien-3-yne in the 1,2-position to form a 7-alkoxy-5-chlorohept-1-en-3-yne (XIII):[63]



The addition of chloromethyl ethers to homologues of hexa-1,5-dien-3-yne, e.g. the 2-methylhexadienyne, is a selective process occurring at the double bond which is richer in electrons: i.e. it takes place by an electrophilic mechanism[64]. Hydrolysis of the resulting vinylacetylenic alkoxy-chloride (XIV) gives the corresponding vinylacetylenic carbinol, which has also been prepared by condensation of the appropriate 2-alkoxyethyl methyl ketone with but-3-en-1-ynyl bromide[65]:



A second molecule of the chloromethyl ether adds to the alkoxy-chloride (XIV) to give a mixture of the two isomeric dichlorides (XV) and (XVI), which with hydrogen chloride in the presence of cuprous chloride produce the same trichloride (XVII):



Certain derivatives of the two dichlorides (XV) and (XVI) have also been obtained[64].

The addition of α-halogeno-ethers to unsaturated compounds opens up great possibilities for the production of new halogen compounds of various types of structure. The ease and simplicity of production of these chlorides allow them to be used as starting materials for the preparation of new insecticides and fungicides, high-boiling solvents, plasticisers, etc. Certain of the α-chloro-ethers and new products obtained from them have already found practical application as insecticides[16,66], water-repellent agents in the textile industry[67,68], and for the treatment of wool to render it stable to washing[69,70].

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THE DEVELOPMENT OF CATALYTIC SYNTHESES OF ORGANIC COMPOUNDS FROM CARBON MONOXIDE AND HYDROGEN

B. K. Nefedov and Ya. T. Eidus

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INTRODUCTION

The catalytic synthesis of hydrocarbons and oxygen-containing compounds from carbon monoxide and hydrogen, particularly on an industrial and semi-industrial scale (Fischer–Tropsch hydrocarbon synthesis, synthesis of alcohols), is of great practical and theoretical interest[1-7]. The most recent reviews in this field were published by one of us in 1950–1951.[1,2] In the present review the main