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Prop-2-ynyl Ethers

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Information on preparation, properties, and practical application is summarised with 306 references.

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I. INTRODUCTION

A prop-2-ynyl (propargyl) ether (the methyl compound) was first obtained by Liebermann in 1865 from glycerol tribromohydrin[1]; its constants were determined by Henry[2]. The next homologue—ethyl prop-2-ynyl ether—was prepared a year later by Bayer[3]. Later the isopentyl[4], phenyl[5], propyl[6], and butyl[7] ethers were obtained. C_{sp}-Halogenated prop-2-ynyl ethers were described as early as 1894.[8] α-Halogeno-ethers of prop-2-ynol were first prepared in 1959.[9] A year later appeared the first paper on propargyl ethers of silanols[10]; those of silylalkanols have not yet been described.

A considerable quantity of information on methods of preparation and chemical behaviour has now accumulated, and indicates that prop-2-ynyl ethers are interesting subjects for investigation. Their peculiar chemical properties are due to the tendency to undergo rearrangements. The prospects for their use in experimental organic chemistry are demonstrated by their employment as starting materials in obtaining the relatively inaccessible allenyl ethers[11], allene hydrocarbons[12], cyclopropane derivatives[13], pyrazoles[14], etc. Prop-2-ynyl ethers are present in several natural materials. According to the patent literature[15] they possess high antibiotic activity.

Propargyl ethers have recently attracted attention in connection with their wide range of useful properties (they have biological activity, help to retard corrosion, aid the flotation of rare metals, and increase the energy content of complicated rocket fuels).

Hitherto, however, hardly any general reviews have appeared on methods of preparation, physical and chemical properties, and applications of this class of heteroatomic acetylenes[16]. The present Review attempts to survey and systematise the information on prop-2-ynyl ethers that has accumulated in the literature.

II. METHODS OF PREPARATION

General methods of preparation of prop-2-ynyl ethers are based on the dehydrohalogenation of halogenoalkyl or halogenoalkenyl ethers[6,17,18] and other elimination reactions[19,20], the action of α-chloroalkyl ethers on metal acetylides[21-24], the alkylation of alkoxides of prop-2-ynols[25-28], the interaction of alkoxides or phenoxides with prop-2-ynyl halides or sulphonates[27,29,30], and the isomerisation of prop-1-ynyl[31] or allenyl[32] ethers.

Alkyl, aryl, and halogenoalkyl prop-2-ynyl ethers have been obtained[17] by the dehydrobromination of 2,3-dibromopropyl ethers in the presence of ethanolic potassium hydroxide:

$$CH_2BrCHBrCH_2OR \xrightarrow[EtOH]{KOH} HC{\equiv}CCH_2OR + KBr \ .$$

This method has no preparative value because of the very low yield (≤ 10%). The ethyl ether cannot be obtained in this way owing to the difficulty of isolating it from the solvent. The aryl ethers can be obtained by the dehydrohalogenation of 1-aroxy-2,2-dihalogenopropanes in the presence of sodamide in liquid ammonia[33]:

$$\underset{X=Cl,\,Br}{ArOCH_2CX_2CH_3} \xrightarrow{NaNH_2/NH_3} ArOCH_2C{\equiv}CH \ .$$

The propyl ether has been obtained[18] by the dehydrochlorination of 3-chloroallyl propyl ether:

$$PrOCH_2CH{=}CHCl \rightarrow PrOCH_2C{\equiv}CH \ .$$

A method of preparation is provided by the alkylation of prop-2-ynols with alkyl arenesulphonates in alkaline media[25]. A convenient methylating agent is dimethyl sulphate, which is highly reactive and quite cheap:

$$HC{\equiv}CCH_2OH + Me_2SO_4 \rightarrow HC{\equiv}CCH_2OMe \ .$$

The ethyl ether is obtained similarly[34].

A simple and convenient procedure is alkylation with prop-2-ynyl halides. Thus the butyl and phenyl ethers have been obtained[7] by the action of prop-2-ynyl bromide on sodium butoxide and phenoxide respectively in ether, when acetylenic–allenic isomerisation is not observed:

$$HC{\equiv}CCH_2Br + RONa \rightarrow HC{\equiv}CCH_2OR \ .$$

A similar method has been used to obtain the tolyl ether[35], by the action of 3-bromopropyne on *p*-cresol in acetone in the presence of potassium carbonate, as well as the allyl[34] and vinyloxyalkyl[36] ethers. It has been recommended[37] to use metallic sodium in liquid ammonia in the alkylation of certain alkynols with benzyl bromide.

The selective alkylation[26-28] of acetylenic alcohols with alkyl halides, first applied to α-acetylenic alcohols, was extended to substituted α- and β-acetylenic alcohols[38]:

$$HC{\equiv}CCOH \xrightarrow[NH_3]{+MNH_2} HC{\equiv}CCOM \xrightarrow{RX} HC{\equiv}CCOR + MX$$
$$R=Bu,\ Cl(CH_2)_n;\ X=Br;\ M=Na,\ K \ .$$

The reaction is complicated by parallel dehydrohalogenation of the alkyl halide with formation of an alkene. The yield

of the prop-2-ynyl ether is 25–80%. The course of the reaction is affected by the nature of the alkyl halide, the alcohol, and the alkali metal; when lithamide is used, the acetylenic hydrogen atom—not the hydrogen atom of the hydroxy-group—is alkylated. The ethyl and butyl ethers (contaminated with allenic isomers) have been obtained by this method in 30% yield[39], and also the methyl ether in 10% yield[40]. The method has been used to obtain the aryl[37], halogenoalkyl, and higher alkyl[41,42] ethers, as well as prop-2-ynyl ethers of secondary and tertiary prop-2-ynyl alcohols[43].

A method of selective alkylation of acetylenic alcohols in the presence of organomagnesium compounds in Hexametapol has recently been worked out[44]. On reaction between ethylmagnesium bromide, an equivalent quantity of 1-bromobutane, and prop-2-ynol at 80–90 °C the hydroxy-group is 80–90% alkylated. With a molar excess of the organomagnesium bromide at 110 °C partial (15–20%) *C*-alkylation occurs. Under these conditions tertiary propargyl alcohols break down with the formation of ketones. The difference in acidity and reactivity between the hydroxyl and acetylenic hydrogen atoms permits successive alkylation of both functional groups or their simultaneous metallation followed by selective alkylation.

Propargyl ethers are obtained also by alkylating prop-2-ynol with alkyl halides in the presence of potassium hydroxide in dimethyl sulphoxide or cyclohexanone[45]. Benzene can be used as solvent in preparing the benzyl and furfuryl ethers[46,47]. Long-chain ethers have been obtained by alkylating prop-2-ynol in the presence of potassium t-butoxide in n-butanol[48]:

$$HC{\equiv}CCH_2OH + C_{18}H_{37}Br \rightarrow HC{\equiv}CCH_2OC_{18}H_{37} .$$

A patent[49] has described the production of ethers from propargyl alcohols and alkyl chlorides in alcoholic solution at 80–150 °C.

The use of propargyl arenesulphonates under mild conditions enables the prop-2-ynyl group to be introduced into various organic compounds (to give 80–95% yields)[50]. The initial sulphonates are obtained by reaction between the sulphonyl chloride and prop-2-ynol in the presence of powdered potassium hydroxide in absolute ether[51]. Interaction between prop-2-ynyl benzenesulphonate and alkoxides yields the corresponding alkyl ethers[52]:

$$PhSO_2OCH_2C{\equiv}CH + RONa \rightarrow ROCH_2C{\equiv}CH .$$

The reaction can be conducted by adding the alkoxide to an alcoholic solution of the sulphonate or by Claisen's method—addition of potassium hydroxide to a solution of the sulphonate and the alcohol—to give 59–60% yields of the ether[51].

The isomerisation of prop-1-ynyl ethers in several cases leads to prop-2-ynyl ethers[31]. Thus in the alkylation of phenol with 3-bromopropyne in the presence of sodamide the resulting ether isomerises into phenyl prop-2-ynyl ether[53]:

$$PhOC{\equiv}CMe \rightarrow PhOCH_2C{\equiv}CH$$

When allenyl ethers are metallated with lithamide in liquid ammonia, they isomerise into prop-2-ynyl ethers[32]:

$$CH_2{=}C{=}CHOR \rightarrow HC{\equiv}CCH_2OR .$$

Diazoalkynes can be used[19] to obtain prop-2-ynyl ethers. *N*-Nitroso-*N*-propargylureas on methanolysis in alkaline medium are converted into a mixture of allenyl methyl and methyl prop-2-ynyl ethers roughly in the proportions 1 : 10:

$$HC{\equiv}CCH(R)-N(NO)-CONH_2 \xrightarrow{MeOH} HC{\equiv}CCH(R)OMe + RCH{=}C{=}CHOMe$$

R = H, Alk .

The decomposition of 1,1,1-trichloro-3-ethoxy-2-trimethylsiloxypropane in the presence of butyl-lithium yields ethyl prop-2-ynyl ether[20]:

$$EtOCH_2CH(OSiMe_3)CCl_3 + 3BuLi \xrightarrow{Et_2O/oxolan} EtOCH_2C{\equiv}CH .$$

The phenyl ether can be obtained similarly (in 25% yield). An attempt to obtain this ether from its "structural components" (ethanol, paraform, and acetylene) in the presence of copper(I) chloride under pressure was unsuccessful[39]:

$$EtOH + CH_2O + CH{\equiv}CH \xrightarrow[25-28\ atm]{Cu_2Cl_2} \begin{cases} \rightarrow EtOCH_2OEt \\ \rightarrow EtOCH_2C{\equiv}CH . \end{cases}$$

At 80 °C reaction does not occur, and at 140 °C diethyl formal is produced.

According to patent claims[30] aromatic propargyl ethers are formed by the action of prop-2-ynyl arenesulphonates on phenols in the presence of bases. Prop-2-ynyl ethers of alkylphenols have been prepared[54] by Claisen's method; it was considered that the duration of the reaction greatly influences the yield, which reaches a maximum after 48 h.

A general method for preparing propargyl ethers is the action of alkyl-, aryl-, and aralkyl-magnesium halides on 1-chloroalkyl prop-2-ynyl ethers[55]. A series of studies[56–58] have shown the possibilities of this method for obtaining the ethers of arylalkanols.

C_{sp}-Silylated propargyl ethers of alkanols, phenols, and diols are obtained by the action of Iotsich reagents on trialkylchlorosilanes[55,56,59,60]:

$$ROCH_2C{\equiv}CMgBr + R'_3SiCl \xrightarrow{Et_3N} ROCH_2C{\equiv}CSiR'_3$$
$$R' = Me, Et .$$

4-Alkoxybut-2-ynyl ethers can be prepared from bisbromomagnesioacetylene and α-halogeno-ethers[21]:

$$BrMgC{\equiv}CMgBr + 2\,ClCH_2OR \rightarrow ROCH_2C{\equiv}CCH_2OR .$$

A promising method suitable for industrial application is the addition of prop-2-ynol to substituted alkenes in acid media:

$$HC{\equiv}CCH_2OH + R_2C{=}CR'_2 \rightarrow HC{\equiv}CCH_2OCR_2CHR'_2 .$$

Its possibilities have not yet been completely revealed because of the limited number of alkenes used in this reaction (fluoroalkenes[61], isobutene[62], norbornenes[63,64]).

Prop-2-ynyl ethers containing a halogen atom adjacent to the triple bond can be obtained by the use of hypohalites[65,66]:

$$HC{\equiv}CCH(R)OR' \xrightarrow{+KOCl} ClC{\equiv}CCH(R)OR' .$$

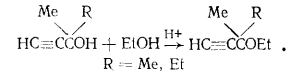
Prop-2-ynyloxyalkyl ethers (formals, acetals) are usually obtained from α-chloroalkyl ethers and prop-2-ynol in the presence of tertiary amines[67,68] or on the contrary from α-chloroalkyl prop-2-ynyl ethers and alcohols[69,70]:

$$\left.\begin{array}{l} HC{\equiv}CCH_2OH + ClCH(R')OR \\ HC{\equiv}CCH_2OCH(R')Cl + ROH \end{array}\right\} \xrightarrow{-HCl} HC{\equiv}CCH_2OCH(R')OR .$$

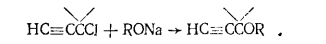
Prop-2-ynyl prop-2-ynyloxyalkyl ethers can also be obtained from prop-2-ynol and aldehydes in the presence of dehydrating agents[71]. Another widely used method for obtaining prop-2-ynyloxyalkyl ethers is the acid-catalysed addition of propargyl alcohols to vinyl ethers[72] and dihydropyran[73]. It is applicable also to the preparation of such ethers of organosilicon alcohols[60].

Tertiary prop-2-ynyl ethers are obtained by different methods from those for the primary ethers. When tertiary propargyl alcohols are heated (at 100 °C for 10 h) with ethanol in the presence of concentrated sulphuric acid, ethyl

tertiary propargyl ethers are obtained[74]:

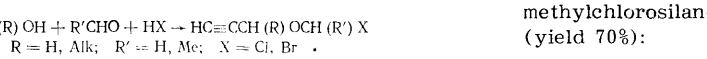


This method can be used also to obtain tertiary homopropargyl ethers[75]. According to patent claims[76] tertiary propargyl ethers are formed by the action of alkoxides on acetylenic tertiary chlorides:

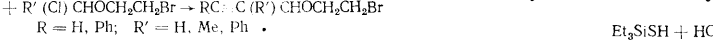


The reaction between acetylenic tertiary alkoxides and alkyl bromides in liquid ammonia gives significantly higher yields[77]. A tertiary benzyl propargyl ether has been obtained similarly; the reaction occurs also in the presence of sodium or sodamide in liquid ammonia[57,58]. Tertiary propargyl ethers are formed also by the alkaline fission of ethers of tetraalkylbutynediols[78] (Favorskii's reaction).

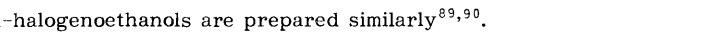
Hologenated ethers are obtained in various ways. Satisfactory yields of 1-chloroalkyl prop-2-ynyl ethers are given by the Henry–Litterscheidt method, by the action of hydrogen chloride or bromide on a mixture of an aldehyde and the alcohol[9]:



The method can be used to obtain C_{sp}-silylated[79-81] and C_{sp}-chloromethylated[82,83] propargyl ethers. When the chlorinating agent is boron trichloride the yield of 1-chloroethyl prop-2-ynyl ether rises[84] to 71%. Three modifications are proposed[85] for this method of obtaining α-halogenoalkyl ethers of primary and secondary propargyl alcohols. 2-Bromoalkyl prop-2-ynyl ethers can be prepared from Iotsich reagents and 1-chloroalkyl 2-bromoalkyl ethers[86]:



2-Halogenoethyl prop-2-ynyl ethers can be obtained from propargyloxyethanol and a halogenating agent (phosphorus tribromide, thionyl chloride)[87,88]:

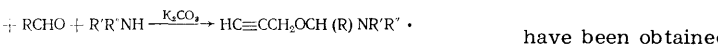


2,2,2-Trichloro-1-halogenoethanols are prepared similarly[89,90]. Prop-2-ynyl ethers containing halogen in the γ, δ, and more remote positions are obtained by alkylating prop-2-ynol with alkylene dihalides in the presence of alkali-metal amides in liquid ammonia[28], utilising the greater polarisability of the carbon–bromide than of the carbon–chlorine bond:



Homopropargyloxyalkyl ethers are formed[91,92] by the action of α-chloroalkyl ethers on terminal β-acetylenic alcohols in the presence of *NN*-dimethylaniline.

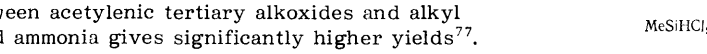
The action of aldehydes and secondary amines on prop-2-ynol forms aminoalkyl ethers[93]:



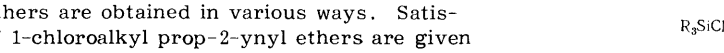
Since aminophenols contain two active centres (amino and hydroxy), their ethers cannot be obtained directly from prop-2-ynyl halides. Aminoaryl ethers are prepared from *N*-acylated aminophenols by the action of 3-bromopropyne in acetone in the presence of potassium carbonate, followed by alkaline hydrolysis[94]. The reaction of propargyl alcohols with acrylonitrile in the presence of sodium methoxide gives 2-cyanoethyl prop-2-ynyl ethers[95]:



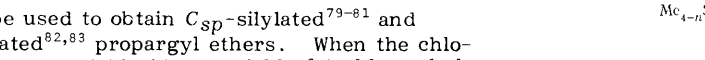
Prop-2-ynyl ethers of silanols (prop-2-ynyloxysilanes) are most often obtained by reaction between trialkylchlorosilanes and propargyl alcohols in the presence of organic bases. The first report[96] that tertiary prop-2-ynyl ethers of trialkylsilanols had been obtained was not confirmed[97,98]. Compounds containing one prop-2-ynyloxy-group attached to the silicon atom were first prepared in 1960 by reaction between prop-2-ynol and monochlorosilanes in the presence of pyridine[10]. Diprop-2-ynyloxysilanes have been obtained from methyldichlorosilane and acetylenic alcohols in the presence of dimethylaniline[99] or triethylamine[100]:



Prop-2-ynyloxysilanes containing aromatic substituents attached to the silicon atom have been prepared similarly[101-103]. 4-Chlorobut-2-ynyloxysilanes have been obtained by reaction between 4-chlorobut-2-ynol and monochlorosilanes[104]:



Si-Chloromethylated ethers are formed from chloromethyldimethylchlorosilane and propargyl alcohols[105]. Ethers of methylsilanols have been obtained[106] from the corresponding methylchlorosilanols and prop-2-ynol in the presence of urea (yield 70%):



Tetraprop-2-ynyloxysilane has been obtained by the transesterification of tetramethoxysilane with a considerable excess of prop-2-ynol in the presence of toluene-*p*-sulphonic acid, which enables formation of a difficultly separable mixture of methoxy-prop-2-ynyloxysilanes to be avoided[106]. The prop-2-ynyl ether of triethylsilanol can be obtained in 60–70% yield from triethylsilanethiol and prop-2-ynol[107]:

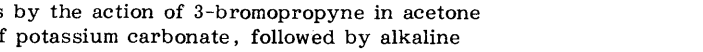
Tertiary propargyl ethers of silanols can be obtained also[108] by the uncatalysed reaction between prop-2-ynols and aminosilanes, which involves fission of the silicon–nitrogen bond, in contrast to the reaction with alkanols:

The dehydrocondensation of propargyl alcohols with alkyl(aryl)silanes also yields ethers of silanols[109]:

Ethers containing a siloxane group of the type

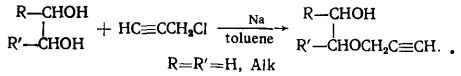


have been obtained by the dehydrocondensation of prop-2-ynol with tetra-alkyldisiloxanes in the presence of zinc chloride in benzene[110]:

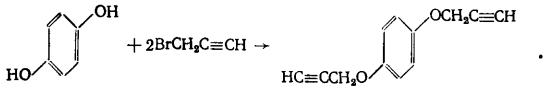


Prop-2-ynyl ethers of glycols can be prepared in various ways. A general method for obtaining partial ethers involves reaction between 3-chloropropyne and monosodio-derivatives

of diols[111]:



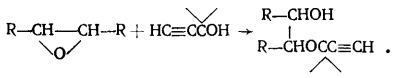
Ethers of polyhydric phenols are obtained by the action of 3-bromopropyne on the phenols[112]:



Mono- and di-ethers of quinol can be obtained by varying the quantities of alkaline component and aryl halide[112]. Prop-2-ynyl ethers containing a vinyl group have been prepared by the reaction[36]

$$CH_2{=}CHO(CH_2)_nONa + BrCH_2C{\equiv}CH \rightarrow CH_2{=}CHO(CH_2)_nOCH_2C{\equiv}CH \quad n=1{-}3 .$$

A convenient route to the monoethers of vicinal glycols is the reaction between propargyl alcohols and symmetrically substituted oxirans in the presence of catalytic quantities of Lewis acids[111,113–119]:



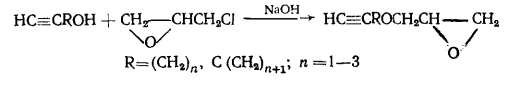
Boron trifluoride etherate[120], a trialkyl phosphite[121], or tin tetrachloride[122–124] can be used as catalyst. The method is restricted to symmetrical oxirans because fission of the epoxide ring is non-selective[125,126]. Furthermore, epichlorohydrin is almost quantitatively and selectively cleaved with the formation of primary monoprop-2-ynyl ethers[122–124,127]. The monoether of ethylene glycol is obtained from prop-2-ynol and 2-chloroethanol in the presence of potassium[120] or sodium[128] hydroxide:

$$ClCH_2CH_2OH + HC{\equiv}CCH_2OH \xrightarrow{-HCl} HOCH_2CH_2OCH_2C{\equiv}CH .$$

It can also be prepared from 3-bromopropyne and ethylene glycol[129]. Monoethers of 2,2,2-trihalogenoethanediols are readily obtained by the reaction of chloral or bromal hydrate with various propargyl alcohols in the presence of hydrochloric acid[89,130]:

$$CH(OH)_2 + HC{\equiv}CCRR'OH \rightarrow CX_3CH(OH)OCRR'C{\equiv}CH$$
$$X=Cl, Br;\ R=R'=H, Alk;\ R=Alk,\ R'=Ar .$$

The cleavage of 2,2-disubstituted 1,3-dioxolans by phenethynyl-, but-3-enynyl-,[131] and prop-2-ynyl-magnesium bromides[132] leads to the formation of γ-substituted tertiary propargyl ethers of ethylene glycol; the reaction of prop-2-ynylmagnesium bromide with 1,3-dioxolans is accompanied by transformation of the terminal triple bond into a disubstituted bond. Propargyl ethers of glycidol are obtained by the action of epichlorohydrin on acetylenic alcohols in the presence of alkali[133] or the ether complex of boron trifluoride[127]:



Phosphorus-containing propargyl ethers are usually obtained from the corresponding phosphorus acid chlorides in the presence of tertiary amines[134,135]:

$$n\,HC{\equiv}CCH_2OH + R_{3-n}PCl \xrightarrow[-n\,HCl]{Et_3N} R_{3-n}P(OCH_2C{\equiv}CH)_n \quad n=1,2 .$$

On standing the ethers are converted into the isomeric allenyl and prop-1-ynyl ethers[136].

C_{sp}-Substituted ethers are prepared by the action of Iotsich reagents obtained from propargyl ethers on alkyl[44], aryl, and hetaryl[137] halides, as well as by the alkylation of prop-2-ynyl ethers with alkyl halides in the presence of sodamide in liquid ammonia[138,139]. A general method for obtaining such substituted ethers is the reaction between acetals and Iotsich reagents based on monosubstituted alkynes[140]:

$$R'R''C(OEt)_2 + RC{\equiv}CMgBr \rightarrow EtOCR'R''C{\equiv}CR .$$

The γ-alkylated ethers can be obtained by the action of alcohols on 1-alkyl-1,3-dichloropropenes in dimethyl sulphoxide at 130–140 °C[141]:

$$ClCH_2CH{=}C(Cl)Me + ROH \xrightarrow[-2HCl]{} ROCH_2C{\equiv}CMe .$$

The action of alkylmagnesium halides on 4-bromobut-2-ynyl ethers also yields 3-alkylated propargyl ethers[142]. A high yield of 3-phenylprop-2-ynyl vinyl ether is formed on the vacuum distillation of bisphenylprop-2-ynyl acetal in the presence of ammonium dihydrogen phosphate[143]:

$$(PhC{\equiv}CCH_2O)_2CHMe \xrightarrow{\Delta} PhC{\equiv}CCH_2OCH{=}CH_2 .$$

1,3-Diphenylprop-2-ynyl ethers can be obtained in good yields[144,145] by heating acetals of aromatic or heterocyclic aldehydes with phenylacetylene in the presence of zinc chloride.

III. PHYSICOCHEMICAL AND SPECTROSCOPIC PROPERTIES

The boiling points of individual branched-chain homologous prop-2-ynyl ethers, in contrast to those of the corresponding alcohols, increase from the primary to the secondary and then to the tertiary ether.

The dipole moments of prop-2-ynyl ethers, unlike those of the corresponding halogeno-derivatives, exceed those of the allyl and propyl ethers, which is explained by a reversal in the direction of the dipole[146]. The inductive constant of the prop-2-ynyloxy-group $\sigma^*(CH{\equiv}CCH_2O) = 2.18$ is almost treble that for the prop-2-ynyl group[147]. Quantum-chemical models of prop-2-ynol and of the prop-2-ynyloxy-anion give a clear idea of the distribution of charges among the atoms and of the strengths of the bonds[148].

Prop-2-ynyl ethers are less basic than the corresponding allyl and propyl ethers because of the decrease in the $+I$ effect in the sequence propyl < allyl < prop-2-ynyl. The centre of maximum basicity in prop-2-ynyl ethers is the oxygen atom. In isostructural ethers $CH{\equiv}CEl(CH_3)_2OCH_3$ the oxygen atom is rather more basic when El = Si than C, which is attributed to $d_\pi-p_\pi$ interaction in the opposite direction to the inductive effect[149]. The oxygen atom is less basic in prop-2-ynyl ethers of silanols than in the saturated analogues, owing to the $-I$ effect of the prop-2-ynyl group and its π-electron-accepting power. 2,2-Dichlorovinyl prop-2-ynyl ether is more basic than the corresponding allyl compound[150].

The presence of intense characteristic absorption bands[151–155] makes it possible to use infrared spectroscopy for the reliable identification of prop-2-ynyl ethers or their detection in a mixture of unsaturated compounds. The spectra of these compounds contain bands characteristic of ≡C–H and C≡C bonds[156,157]. Stretching vibrations of the former bond produce a band in the range 3295–3320 cm^{-1}; the band in the region of 600 cm^{-1}, caused by deformation vibrations (overtone 1200 cm^{-1}), is unsuitable for analytical purposes, since other functional groups are able to absorb in these regions. For the same reasons caution is necessary in the interpretation of structure by means of the band at 1325–1336 cm^{-1},

which is ascribed[158] to angular vibrations of the methylene group in the prop-2-ynyl fragment. Greater importance attaches to the weak band due to the acetylenic bond, which usually appears in the frequency range 2110–2130 cm^{-1}.

A recent study of the infrared spectra of prop-2-ynyl ethers has provided direct evidence of the absence of conjugation through the methylene bridge between the lone electron pair of the oxygen atom and the π electrons of the triple bond[159]. Study of the Raman, ultraviolet, and nuclear magnetic resonance spectra also indicates absence of $p-\pi$ conjugation[160].

The signals from acetylenic protons in the ^1H n.m.r. spectra of alkyl prop-2-ynyl ethers appear down-field relative to those of α-alkoxyacetylenes. The ^1H n.m.r. spectra[161–163] of prop-2-ynyl ethers containing a $CH{:}CCH_2O$ fragment exhibit a triplet in the range $\delta = 1.4–2.2$ ppm (:CH protons) and a doublet at 4.05–4.25 ppm (protons of the $:CCH_2$ group). The characteristic spin–spin coupling constant is 2–3 Hz.[164]

In order to investigate the possibility of hydrogen bonding, chemical shifts of the signal from the acetylenic proton in the n.m.r. spectra of alkyl prop-2-ynyl ethers and their non-oxygen analogues have been measured in concentrated solutions and on dilution with inert or proton-donor solvents[165]. The presence of oxygen causes a considerable shift in the signal, as a consequence of formation of a hydrogen bond with the oxygen atom.

A study has been made of the dependence of the mass-spectrometric fragmentation of substituted phenyl prop-2-ynyl ethers on the nature of the cyclic substituents[166]. In several ethers (e.g. the phenyl ether itself) electron bombardment produces skeletal rearrangements with the loss of carbon monoxide and formation of the $[M-CO]^+$ ion, which has not yet found a theoretical interpretation[167]. In this respect it is interesting that the carbon monoxide molecule is among the stable neutral species most often eliminated in rearrangements of aromatic compounds. The mass spectra of tertiary propargyl ethers of ethanol have been examined[168].

IV. REACTIVITY

Prop-2-ynyl ethers undergo diverse reactions involving the acetylenic hydrogen atom, the triple bond, and also the ethereal oxygen atom. Their reactivity is due not only to the actual nature of the acetylenic bond but also to the presence of the electron-accepting ether group[169,170].

1. Rearrangement

Prop-2-ynyl ethers undergo various rearrangements with the formation of isomeric compounds. Thus the methyl ether isomerises into allenyl methyl ether when heated with solid caustic potash[171]; sodium methoxide in dimethyl sulphoxide has a similar effect[172]:

$$MeOCH_2C{\equiv}CH \rightarrow MeOCH{=}C{=}CH_2 .$$

The n.m.r. spectra show that the mixture does not contain even traces of methyl prop-1-ynyl ether. The latter does not form the allenyl ether under the influence of sodium methoxide in the presence of dimethyl sulphoxide, which implies that it is more stable than the prop-2-ynyl ether[172]. Rearrangement does not take place in the formation of ethers from the corresponding acetylenic chlorides and alcohols in the presence of alkalis[173,174], nor in the replacement of halogen in various prop-2-ynyl halides by means of alkoxides[7].

A method of preparing allenyl ethers[11] was based on the isomerisation of prop-2-ynyl ethers in the presence of potassium t-butoxide:

$$HC{\equiv}CCH_2OR \rightarrow CH_2{=}C{=}CHOR .$$

The allenyl ether is readily metallated by butyl-lithium:

$$CH_2{=}C{=}CHOR + BuLi \rightarrow CH_2{=}C{=}C(Li)OR .$$

When an ether is alkylated with an alkyl halide in liquid ammonia, a mixture of allenyl and prop-2-ynyl ethers is formed, whereas alkylation in an oxolan–ether mixture gives only α-alkylallenyl ethers. The action of organomagnesium compounds on prop-2-ynyl ethers in the presence of cuprous bromide yields allene hydrocarbons[12]:

$$MeOCRR'C{\equiv}CR'' + R'''MgBr \xrightarrow{Cu_2Br_2} RR'C{=}C{=}CR''R''' .$$

Under the influence of aldehydes or ketones in the presence of potassium hydroxide alkyl and aryl prop-2-ynyl ethers give mixtures of acetylenic ether–alcohols and allenyl ethers[172]:

$$PhOCH_2C{\equiv}CH + RCHO \xrightarrow[DMF]{KOH} \begin{cases} \rightarrow PhOCH_2C{\equiv}CCH(R)OH \\ \rightarrow PhOCH{=}C{=}CH_2 \end{cases} .$$

Similar isomerisation of prop-2-ynyl ethers in alkaline medium has been observed by several workers[175,176].

Alkynyl 2-bromoalkyl ethers, on dehydrobromination in the presence of sodamide in a liquid ammonia, undergo partial rearrangement into the corresponding prop-2-ynyl ethers. However, several workers[177] cast doubt on the isomerisation of terminal acetylenic compounds under the influence of this reagent. A tendency to prototropic isomerisation of aryl prop-2-ynyl ethers has been observed also under the influence of alcoholic alkali[33] or potassium t-butoxide[178]. For example, the preparation of prop-2-ynyl ethers from the bromides involves formation of a mixture of prop-2-ynyl, allenyl, and prop-1-ynyl ethers:

$$BrCHR''C{\equiv}CR' + ROM \longrightarrow \begin{cases} \rightarrow ROCHR''C{\equiv}CR' \\ \rightarrow ROCR''{=}C{=}CHR' \\ \rightarrow ROC{\equiv}CCH_2R' \end{cases}$$

R=Alk, Ar; R'=H, Alk, Ar; R''=H, Alk .

Attempts to effect the rearrangement of phenyl and naphthyl prop-2-ynyl ethers under the conditions of the Claisen reaction were unsuccessful[179].

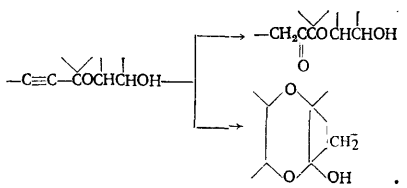
2. Addition

The most characteristic property of prop-2-ynyl ethers is their ready ability to undergo quantitative hydration to ether–ketones. Thus gentle heating of the methyl ether with water in the presence of mercury(II) sulphate forms methoxyacetone[25]:

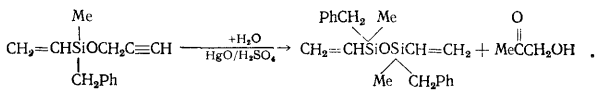
$$HC{\equiv}CCH_2OMe + H_2O \xrightarrow{HgSO_4} MeCOCH_2OMe .$$

A rapid and convenient method has been developed[45] for the catalytic hydration of prop-2-ynyl ethers to the corresponding ethers of hydroxyacetone. Other alkyl prop-2-ynyl ethers have also been subjected to hydration, as well as those containing aromatic, alicyclic, and heterocyclic groups[17,37,139]. The monoethers of α-glycols undergo hydration in two ways determined by the polar and steric effects of substituents,

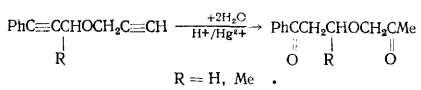
mainly in the prop-2-ynyl fragment[180-182]:



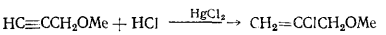
Hydration of the ethers of silanols in the presence of a mixture of mercuric oxide and sulphuric acid is accompanied by rupture of the silicon–oxygen bond, with formation of the corresponding disiloxane and hydroxyacetone[103]:



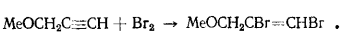
The hydration of prop-2-ynyl ethers of phenylprop-2-ynols gives phenacylalkyl ethers of hydroxyacetone[182]:



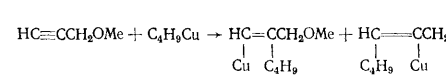
A monoadduct is obtained by the action of concentrated hydrochloric acid on methyl prop-2-ynyl ether in the presence of mercury(II) chloride[183]:



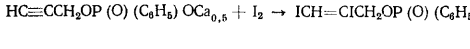
The catalytic effect is due to the formation of complexes with hydrogen chloride, not intermediate organomercury compounds. The kinetics of the addition of elementary bromine to the methyl ether



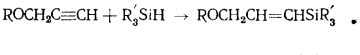
indicates a termolecular process[184]. A kinetic study has been made also of the addition of mercuric chloride to the methyl ether in the presence of lithium chloride[185]. Addition of a copper alkyl to a prop-2-ynyl ether[186] gives a mixture of isomers:



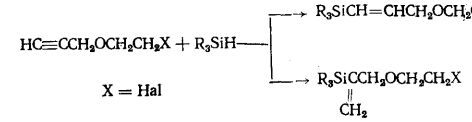
The organophosphorus esters smoothly add iodine[187]:



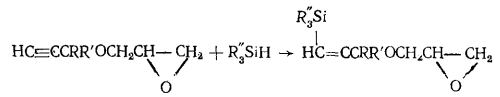
In the presence of a Speier catalyst prop-2-ynyl ethers readily undergo hydrosilylation[188]:



With hydroxylated ethers under these conditions the process is unaccompanied by dehydrocondensation: i.e. the hydroxy-group is unaffected[75]. Halogenated ethers give mixtures of isomeric adducts without involving the halogen atom[189]:



In the hydrosilylation of tertiary prop-2-ynyl ethers of chloral hydrate, however, products of addition at the multiple bond are accompanied by those in which chlorine atoms of the trichloromethyl group have been replaced by a trialkylsilyl radical[190]. The epoxide ring is preserved when prop-2-ynyl ethers of glycidol undergo hydrosilylation[124,127,191-193]:



Prop-2-ynyl ethers are readily hydrogenated in the presence of Raney nickel[137], palladium[139], and also platinum[57] catalysts, whose activity is the main factor determining the reaction velocity. For example, the rate of hydrogenation of the monoether of ethylene glycol on a nickel–molybdenum catalyst exceeds by a factor of 13 the rate when Raney nickel is used under the same conditions[194]. Platinum black can be used[57] for the exhaustive hydrogenation of a tertiary propargyl ether of benzyl alcohol. In the presence of a palladium catalyst deactivated with lead acetate the triple bond is hydrogenated to a double bond[195]:

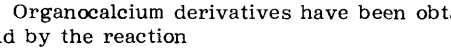


3. Substitution

(a) Reactions with Metals

The tendency of prop-2-ynyl ethers to undergo substitution is evident primarily in their reactions with metals and organometallic compounds. The acetylenic hydrogen atom is readily replaced by a heavy metal. On treatment with ammoniacal silver nitrate white precipitates of silver salts separate. Cuprous chloride solution gives yellow precipitates of copper(I) salts.

Sodium derivatives of the ethers should be prepared by means of sodamide in liquid ammonia[196]. Lithium derivatives are obtained from butyl-lithium and the ether in diethyl ether[197]. Organocalcium derivatives have been obtained[198] in 90% yield by the reaction



Organomagnesium derivatives of prop-2-ynyl ethers (Iotsich reagents) are smoothly formed in ether or oxolan[199], and will react with almost all the reagents that undergo organomagnesium synthesis[137,197-201]. The reactions of the magnesium derivatives have been studied most thoroughly. Methyl prop-2-ynyl ether in its reactions with organomagnesium compounds is more active than hex-1-yne by a factor of almost 12,[169] which is explained by the ability of the oxygen atom to attract electrons and thereby to increase the mobility of the acetylenic hydrogen atom.

(b) Reactions with Carbonyl Compounds

Organomagnesium derivatives of prop-2-ynyl ethers are widely used for the synthesis of acetylenic ether–alcohols. When aldehydes and ketones are treated with Iotsich reagents obtained from these ethers, the corresponding secondary and tertiary ether–alcohols are formed. Iotsich reagents from alkyl prop-2-ynyl ethers give alcohols in 60–70% yields[199]. The methyl ether with aldehydes forms ether–alcohols in 60% yield[199,202]:

Similarly, 5-phenoxypent-3-yn-2-ol has been obtained (yield 50%) from phenyl prop-2-ynyl ether, iodoethane, and acetaldehyde[201].

Prop-2-ynyl ethers are able to react with aldehydes and ketones also under the conditions of the Favorskii reaction. The ethyl ether condenses with diphenyl ketone in the presence of potassium hydroxide in oxolan even at room temperature[203]:

$$HC{\equiv}CCH_2OEt + Ph_2CO \rightarrow EtOCH_2C{\equiv}C\overset{Ph\ \ Ph}{\diagup\diagdown}COH \ .$$

The propyl and butyl ethers condense smoothly with various ketones[18,39,204,205] and alcoholic ketones[29,206].

The condensation of prop-2-ynyl ethers with carbonyl compounds takes place also in liquid ammonia[207]. Thus the methyl ether reacts with benzaldehyde to give a 68% yield of 1-phenylbut-2-yne-1,4-diol.

Organomagnesium derivatives of alkyl prop-2-ynyl ethers are carboxylated by means of dialkyl carbonates[208,209] and oxalates[40] in ethereal solvents, being converted into the corresponding alkoxybutynoic esters. With α-chloroalkyl ethers the magnesium derivatives form γ-substituted alkoxyalkyl prop-2-ynyl ethers[197], and with orthoesters acetals are formed[73].

(c) Other Substitutions

In liquid ammonia the Iotsich reagents are readily alkylated by alkyl bromides[137,138].

On treatment with hypohalites the acetylenic hydrogen atom in the ethers is replaced by halogen[8,66]:

$$ArOCH_2C{\equiv}CH + NaOX \rightarrow ArOCH_2C{\equiv}CX$$
$$X = Cl,\ Br \ .$$

The halogen in the products can easily be substituted[66]:

$$ArOCH_2C{\equiv}CBr + HC{\equiv}CCH_2\overset{O}{\overset{\|}{C}}CH{=}CH_2 \rightarrow ArOCH_2C{\equiv}CC{\equiv}CCH_2\overset{O}{\overset{\|}{C}}CH{=}CH_2 \ .$$

The action of a copper(I) salt and ammonium chloride on the ethers yields diethers of "head to head" type[210]:

$$ROCH_2C{\equiv}CH \xrightarrow{Cu_2Cl_2+NH_4Cl} (ROCH_2C{\equiv}C{-})_2$$
$$R{=}Me,\ Et,\ Pr,\ Bu \ .$$

Dehydrodimerisation takes place also in the oxidative condensation of *p*-ferrocenylphenyl prop-2-ynyl ether[211] in a mixture of ether, pyridine, and methanol (2 : 2 : 1) in the presence of copper salts[212]:

$$\pi\text{-}C_5H_5FeC_5H_4C_6H_4OCH_2C{\equiv}CH + HC{\equiv}CR \rightarrow \pi\text{-}C_5H_5FeC_5H_4C_6H_4OCH_2C{\equiv}CC{\equiv}CR$$
$$R{=}Ph,\ CH_2OH,\ C_5H_5FeC_5H_4 \ .$$

Under certain conditions stannyl chlorides[196] and stannanols[213] react with alkyl prop-2-ynyl ethers with substitution of the acetylenic hydrogen atom by a trialkylstannyl group:

$$ROCH_2C{\equiv}CH + Alk_3SnX \rightarrow ROCH_2C{\equiv}CSnAlk_3$$
$$X{=}Cl,\ OH \ .$$

(d) Aminomethylation

Prop-2-ynyl ethers react under the conditions of the Mannich reaction with formaldehyde and secondary amines to form the aminomethylated ethers[25,35,47,55,139,214–216]:

$$ROCH_2C{\equiv}CH + CH_2O + R'_2NH \rightarrow ROCH_2C{\equiv}CCH_2NR'_2 \ .$$

The reaction is usually conducted in the presence of copper(I) chloride in dioxan. Copper acetate has also been proposed as catalyst[139].

The uncatalysed aminomethylation of hydroxylated ethers involves the hydroxyl hydrogen atom[217]:

$$HC{\equiv}CCOCH_2CH_2OH + CH_2O + R_2NH \rightarrow \diagup\diagdown C\overset{C{\equiv}CH}{\underset{OCH_2CH_2OCH_2NR_2}{\diagup\diagdown}} \ .$$

Preliminary chemical protection of the hydroxy-group enables this undesirable process to be suppressed and the desired products to be obtained[218]. Aminomethylation of the monoethers of ethylene glycol in the presence of cuprous chloride involves the ethynyl hydrogen atom without affecting the hydroxyl hydrogen[219].

Results have been published[101] indicating the possibility of obtaining C_{sp}-aminomethylated derivatives of prop-2-ynyl ethers of silanols:

$$PhCH_2SiMe_2OCH_2C{\equiv}CH + CH_2O + R_2NH \rightarrow PhCH_2SiMe_2OCH_2C{\equiv}CCH_2NR_2 \ .$$

The aminomethylation of the halogenated ethers does not involve the halogen atom[205]:

$$HC{\equiv}CCH_2O\overset{R\ \ R'}{\overset{|\ \ \ |}{C}}HCHCl + CH_2O + Et_2NH \rightarrow Et_2NCH_2C{\equiv}CCH_2O\overset{R\ \ R'}{\overset{|\ \ \ |}{C}}HCHCl \ .$$

(e) Reactions of Halogenated Ethers Involving the Halogen Atoms

Under certain conditions halogen atoms present in prop-2-ynyl ethers can be replaced by various groups. Thus prop-2-ynyl acetals of aldehydes are formed by reaction of the chloroalkyl ethers with alcohols[220–222]:

$$ROH + ClCHOCH_2C{\equiv}CH \rightarrow ROCHOCH_2C{\equiv}CH$$
$$\quad\ \ |\qquad\qquad\qquad\quad\ \ |$$
$$\quad\ R'\qquad\qquad\qquad\quad\ R'$$
$$R{=}\ H_2C{=}CH,\ C_6H_{13};\ R'{=}H,\ Me \ .$$

1- and 2-Halogenoalkyl prop-2-ynyl ethers react readily with Iotsich reagents obtained from monosubstituted acetylenes[86] and also with alkali-metal alkoxides[223].

Investigation of the behaviour of mono- and di-halogenated prop-2-ynyl ethers towards various nucleophiles has provided an experimental basis for a suggested activity series of halogen atoms depending on polar and steric factors. This can be used in directed syntheses of technically valuable products[223].

Tertiary propargyl ethers of 1,2,2,2-tetrachloroethanol are dehalogenated in the presence of zinc with the formation of dichlorovinyl prop-2-ynyl ether[224]:

$$CCl_3\overset{Cl\ R}{\overset{|\ \ \diagdown}{C}}HOC\overset{R}{\overset{\diagup}{\equiv}}CH \xrightarrow[-Cl_2]{Zn} CCl_2{=}C\overset{R\ \ R}{\overset{\diagup\ \ \diagdown}{\ }}OCC{\equiv}CH \ .$$
$$R{=}H,\ Me$$

Subsequent addition of prop-2-ynol yields the diprop-2-ynyl acetal of 2,2-dichloroacetaldehyde:

$$CCl_2{=}C\overset{H\ \ H}{\overset{\diagup\ \ \diagdown}{\ }}OCC{\equiv}CH + HOCH_2C{\equiv}CH \xrightarrow{H^+} CHCl_2CH\,(OCH_2C{\equiv}CH)_2 \ .$$

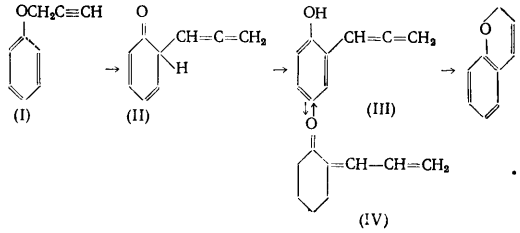
Organosilicon alkoxyalkenynes have been obtained[225] by the dehydrohalogenation of 3-silylated prop-2-ynyl ethers containing a 1-bromomethyl group:

$$Me_3SiC{\equiv}C\overset{CH_2Br}{\overset{|}{C}}HOR \rightarrow Me_3SiC{\equiv}C\overset{CH_2}{\overset{\|}{C}}OR \ .$$

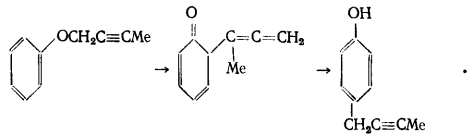
4. Cyclisation

The special synthetic value of prop-2-ynyl ethers consists in the possibility of transforming them into various difficultly accessible carbocyclic and heterocyclic compounds.

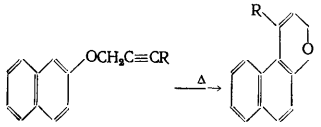
The unique scheme proposed[226] for the cylisation of the aryl ethers involves the formation, from the phenyl ether (I) as example, of the allenyl-dienone (II) (rate-determining stage) followed by rapid enolisation into allenylphenol (III), sigmatropic migration of hydrogen with conversion into (IV), and cyclisation to chromen:



In the case of but-2-ynyl phenyl ether the intermediate methylallenyl-dienone rearranges into but-2′-ynylphenol:

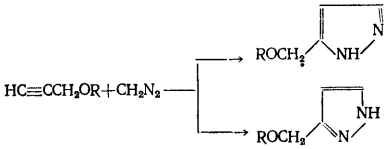


The thermal cyclisation of 4-phenoxybut-2-ynyl phenyl ether forms phenoxymethylbenzopyran[227]. The C_{sp}-substituted naphthyl ethers cyclise in the presence of diethylaniline into the corresponding naphthopyrans[228]:



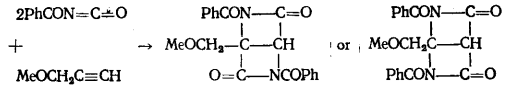
The reaction involves a Claisen rearrangement. Phenyl prop-2-ynyl ethers when heated also undergo a sigmatropic rearrangement with formation of the corresponding chromens[229]. The cyclisation of aliphatic propargyl ethers has been described[230-233].

Examples are known of cyclisation in reactions with various types of dipoles. A method for obtaining alkoxylated pyrazoles is based on interaction with diazoalkanes[14]:

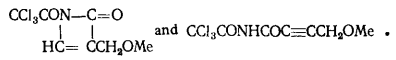


The reaction involves intermediate formation of the zwitterion $^{+}N_2CH_2CH{:}C^{-}R$, the uniform charge separation in which is confirmed by absence of a solvent effect on the proportions of isomers formed.

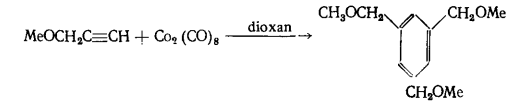
Prop-2-ynyl ethers have been subjected to intermolecular cyclisation with benzoyl and trichloroacetyl isocyanates[170]. The benzoyl compound and the methyl ether in diethyl ether at 0 °C give a product which was regarded as a diadduct:



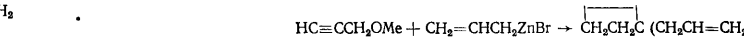
Trichloroacetyl isocyanate reacts far more slowly; under severe conditions a mixture of isomers of cyclic and linear structure is obtained:



Methyl prop-2-ynyl ether undergoes cyclisation to an alkoxymethylquinol under the influence of iron carbonyls[234]. Similarly, trimerisation with formation of a mesitylene derivative occurs on heating in an organic solvent in the presence of a metal carbonyl[235]:

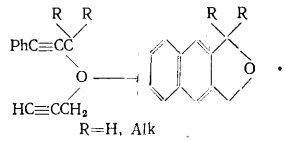


1,1-Diallylcyclopropane has been synthesised by the addition of allylzinc bromide to the methyl ether[13]:



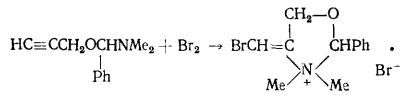
Replacement of methyl by phenyl facilitates cyclisation and increases the yield of the desired product.

Intramolecular cyclisation of phenylprop-2-ynyl prop-2-ynyl ethers in *p*-xylene yields naphtho-oxolans[236]:



The thermal cyclisation of C_{sp}-substituted prop-2-ynyl ethers forms 2*H*-chromens in 60% yield[237].

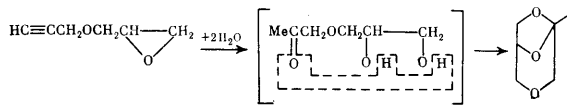
The bromocyclisation of α-dimethylaminobenzyl prop-2-ynyl ether yields 4-bromomethylene-3,3-dimethyl-2-phenyloxazolidinium bromide:



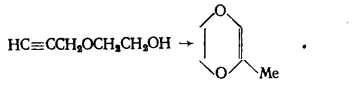
2-Halogenoalkylated prop-2-ynyl ethers are used in the synthesis of difficultly accessible prop-2-ynylated 1,4-dioxans[238].

A cyclobutene derivative is formed in the photochemical addition of methyl prop-2-ynyl ether to vinylene carbonate[239]. The catalytic oligomerisation of butadiene with alkynyl prop-2-ynyl ethers leads to the formation of 4,5-disubstituted cyclodeca-1,4,7-trienes[240].

Cyclisation of the prop-2-ynyl ether of glycidol gives trioxabicyclo-octane[241], presumably with intermediate formation of an acetonyl ether of glycerol, which cyclises by intramolecular acetalisation:



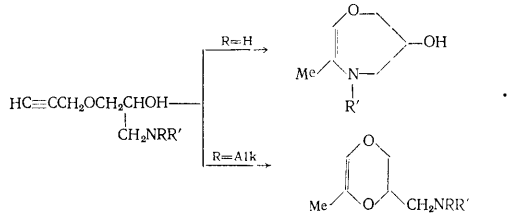
Cyclisation of the ethers of vicinal diols has been studied[111, 120, 129]. Prop-2′-ynyloxyethanol in 2-ethoxyethanol in the presence of potassium hydroxide forms 2,3-dihydro-5-methyl-1,4-dioxin[120]:



Cyclisation of the ethers of alkylated ethylene glycols gives mixtures of alkylated dihydro-1,4-dioxins, isomeric heterocycles with an exocyclic double bond, and vinylated 1,3-dioxolans[111,129]. Under these conditions the cyclisation of

prop-2'-ynyloxycyclohexanol yields geometric isomers of dihydrocyclohexanodioxin.

The direction of the base-catalysed intramolecular cyclisation of monoprop-2-ynyl ethers of aminoalkylated α-glycols is determined by the degree of substitution at the nitrogen atom[242]. Cyclisation of the tertiary amines involves the hydroxy-group and gives dihydroaminoalkyl-1,4-dioxins, but that of the secondary amines involves the nitrogen–hydrogen bond and yields oxazepine derivatives:



V. PRACTICAL APPLICATION

Prop-2-ynyl ethers are continually finding new fields of practical application in addition to their use in organic synthesis. They can be applied as stabilisers for cellulose acetate and goods based thereon (acetate rayon, cinematograph film, plastic materials, etc.), which age under the influence of light, temperature, etc. during service, with a consequent deterioration in their physicochemical properties, premature failure, and wear[243]. Benzyl prop-2-ynyl ether has been proposed as stabiliser to increase the resistance of cellulose acetate to light[244]. Stability towards light is also acquired by lower chlorinated hydrocarbons on the addition of propyl, butyl, isobutyl, isopentyl, and phenyl prop-2-ynyl ethers together with a stabiliser[243].

The ethers with aryl and diaryl groups can serve as monomers for the synthesis of heat-resistant polymers[112]. Oligomers of the type $HO[CH_2C{:}CCH_2OCR(OH)]_nR'$ (R, R' = H, Alk) are used as power-consuming additives for rocket fuels, improving the ballistic properties of the compositions[245].

Several hydroxylated prop-2-ynyl ethers have found application in the synthesis of auxiliary agents for the textile and paper industries[246]. Products of the hydrosilylation of prop-2-ynyl ethers of silanols are used as finishes for textile materials[247]. Monoprop-2-ynyl ethers of ethylene and propylene glycols may find application in electroplating as brightening agents[248]. Dibenzocycloheptatrienes obtained from prop-2-ynyl ethers are employed in the pharmaceutical industry with inert carriers[249].

1. Biological Properties

Many prop-2-ynyl ethers possess biological activity and can be used in agriculture both as toxic chemicals and in veterinary practice to destroy parasites and in the fight against gastric diseases in farm animals[250–252].

The use has been proposed of preparations based on these ethers that destroy arachnoid mites, leaf aphids[253], beetles and rats[252], house-flies[254], nematodes and other parasitic worms in the soil[250]. The compound $I_2C{:}CClCH_2OR$, obtained by the interaction of a prop-2-ynyl ether, chloroform, and iodine, stimulates the growth of poultry[255]. The same preparation has been recommended for use in veterinary practice for the treatment of diarrhoea, and its isologue for the treatment of gastric diseases in pigs[252].

Prop-2-ynyl ethers also possess strong bactericidal and herbicidal properties[256]: the ether of 2',4',6'-tri-iodo-2,4-dinitroazophenol is a more active bactericide than is chloramphenicol[257]. 4-Chlorobut-2-ynyl *m*-chlorophenylcarbamate (Barban) is a herbicide for the post-germination treatment of fine-grained cereals against wild oats[258]. Chlorine-containing C_{sp}-silylated prop-2-ynyl ethers of general formula $ClCH_2Si(CH_3)_2C{:}CCH_2OCHRCH_3$ surpass known standard preparations (chloramine, Rivanol, Nitrofungin) in antibacterial activity[259].

There are indications[256] that prop-2-ynyl ethers may serve as starting materials for the synthesis of diverse bifunctional acetylenes and amino-ethers developing fungicidal activity. Several derivatives are pharmacologically active compounds[260]. A tertiary prop-2-ynyl carbamate (Oblivon C) is used as a mild hypno-sedative agent and has an antispasmodic effect[261]. In contrast to prop-2-ynyl ethers[262] homopropargyl aminoacetates possess a strong soporific–anticonvulsant type of psychotropic activity[263–265].

The C_{sp}-iodinated prop-2-ynyl ether of 2,4,5-trichlorophenol is used therapeutically as an antimycotic and antiseptic[266]. The muscarinic action of the prop-2-ynyl ether of choline is double those of the allyl and propyl analogues[266]. C_{sp}-Aminomethylated derivatives of the monoprop-2-ynyl ether of ethylene glycol[264] and diprop-2-ynyl acetal[265] have a mild hypno-sedative action combined with a muscle-relaxant effect and slight antispasmodic properties. Substances having a general hypno-sedative profile include also prop-2-ynyl ethers of silanols[267,268]. The ethers of glycerol possess spasmolytic properties[260], and those of oxan hypnotic properties[266].

1-Alkylprop-2-ynyl ethers of long-chain alcohols $ROCHR'C{:}CH$ ($R = C_6H_{13}$, C_8H_{17}, etc.) have a beneficial effect on blood formation[269]. Prop-2-ynyl ethers of arylated pyranols have been claimed[270] as pesticides. The tertiary prop-2-ynyl ether of the monochlorohydrin of glycerol $HC{:}CC(CH_3)_2OCH_2CH(OH)CH_2Cl$ (an analogue of Mephenesine) is able to relax muscles[122]. The hypothesis that structures having both propargyl and oxiran groups would probably possess antitumour activity was not supported by an investigation of C_{sp}-substituted prop-2-ynyl ethers of glycidol[123]. However, C_{sp}-aminomethylated tertiary ethers of general formula $ROCR'R''C{:}CCH_2N(CH_2CH_2Cl)_2$ do exhibit such activity[271]. Several hydroxylated prop-2-ynyl ethers are perfumes[272].

2. Protection of Metals from Corrosion

The problem of inhibitors of acid corrosion merits close attention, since the rate of corrosion breakdown and the associated material damage are especially large for most metals particularly in contact with acid media[273–280]. In connection with the increasing demand for inhibitors of the high-temperature corrosion of steel in hydrochloric acid recent years have been the concentration of attention on acetylenic compounds, and the preparation of novel functionally substituted compounds of this class has again occupied a primary position in work on fine organic synthesis.

Even mechanical mixtures of known nitrogen-containing inhibitors with certain acetylenic compounds are found to be quite reliable corrosion inhibitors at high temperatures[281,282]. The position of the triple bond has a very strong influence on the protective effect, which is greatest when the bond is terminal[283]. The protective effects of acetylenic compounds fall in the sequence[284] secondary alcohols > primary alcohols > ethers > sulphides > tertiary alcohols > hydrocarbons. Diacetylenic compounds are more promising than vinylacetylene derivatives[285].

Prolonged tests on acetylenic inhibitors in technical 28% hydrochloric acid have demonstrated the stability of prop-2-ynol and its ethers[286,287]. Alkylcycloalkylphosphonic esters of the type $AlkC_6H_{10}PO(OCH_2C{:}CH)_2$ have proved to be effective inhibitors, protecting metals at temperatures up to 100 °C and above[288-290], with the protective effect depending on the size and structure of the radical[284]. Diprop-2-ynyl sulphide, which is comparatively readily available, also has a strong anticorrosive effect[291]. Diprop-2-ynyl ether is a corrosion inhibitor for ferrous metals and nickel in non-oxidising acids[276].

Prop-2-ynyl ethers of phenols also have a protective effect: for example, that of *m*-cresol inhibits the corrosion of steel in hydrochloric acid more effectively than does prop-2-ynol. The protective effect of the *m*-tolyl ether is weakened when the ethynyl hydrogen is replaced by alkyl[292,293]. In the aromatic series the most effective inhibitors of the corrosion of steel and its absorption of hydrogen in hydrochloric acid have been the prop-2-ynyl ethers of 1- and 2-phenylalkanols and of 3-phenylprop-2-ynol[294-296]; the inhibition coefficient increases steadily with temperature. Introduction of a sulpho-group into the benzene (naphthalene) ring weakens the inhibiting properties of the derived ethers[297].

The protective effect of prop-2-ynyl ethers of silanols is determined mainly by the action of products of acid hydrolysis[295]. Among complete and partial prop-2-ynyl and prop-2'-ynyloxyalkyl ethers of glycols the most effective and stable properties are exhibited by diprop-2-ynyl ethers, in particular by that of ethylene glycol[298,299]. Prop-2-ynyl esters of aliphatic acids are less effective corrosion inhibitors than are the corresponding ethers of alcohols and phenols[300]. The introduction of amino-radicals into the ethers considerably diminishes the inhibiting effect[299,300].

Many investigators have been concerned to elucidate the mechanism of the inhibiting effect of acetylenic compounds on acid corrosion[301-306]. An adsorption–polymerisation mechanism is consistent with established laws. Most research workers have shown that the protective action of terminal acetylenes is due to polymerisation by opening of the triple bond, leading to formation of a protective polymer film on the metal surface[301,304]. However, Japanese workers consider[305] that the protective effect of acetylenic compounds is due rather to adsorption than to formation of a polymer film. Acetylenic compounds are adsorbed on iron by means of the triple bonds[278], forming π complexes with the metal, with a consequent positive displacement of the potential on the *I* scale.

Since the mechanism of the protective action of acetylenic compounds in the acid corrosion of metals still remains an open question, further study is required of the influence of their structure on their inhibiting effect.

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