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Propargyl Compounds in the Synthesis of Carbocycles and Heterocycles

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Data on the conversion of propargyl compounds into carbocycles and heterocycles are surveyed. The bibliography includes 181 references.

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I. INTRODUCTION

The cyclisation reactions of propargyl compounds have been the object of a comprehensive study in view of their importance for theoretical and synthetic organic chemistry. The characteristic features of the cyclisation of propargyl compounds are in many respects determined by their tendency to undergo rearrangements, Michael addition reactions, and diene and carbene syntheses.

The increased interest in the cyclisation of propargyl compounds is caused, apart from the need to solve theoretical problems, by their enormous role in the synthesis of carbocycles and heterocycles otherwise difficult to obtain, which can serve as the starting materials for the preparation of natural products and medicinal drugs.

Derivatives of isoquinolines[1], pyrimidines[2], pyranoflavans[3], and pyranoacridones[4], which occur in natural condensed systems, many vitamins, and antibiotics, have been obtained from propargyl compounds. For example, we may note the synthesis of a natural antibiotic—the lactone of 4-hydroxy-2-vinyl-but-2-enoic acid—from propargyl vinyl ether[5], of hydroxypyrones with a broad spectrum of biological activity from propargylvinyl alcohols[6], of aryldihydroisoquinolines, which are intermediates in the synthesis of alkaloids, from propargylbenzylamines[1], and of oxazoles, which are intermediates in the synthesis of vitamins B_6, from *O*-propargyliminoesters[7]. The antihypertonic activity of *N*-(guanidinoalkyl)pyrrolidines, synthesised from tertiary homopropargyl alcohols[8], has been noted and synthetic lignan lactones have been obtained by the intramolecular diene synthesis from propargyl propiolates[9].

In view of the undoubted practical value of acetylenic compounds of this type, there has been a considerable growth in interest in their cyclisation reactions in recent years. A monograph[10] and a number of reviews[11-16] have been published on the chemistry of acetylenic compounds, but they do not deal with the problem under consideration in terms of the cyclisation of propargyl compounds. In the present review an attempt is made to arrange systematically the studies in the last ten years on the cyclisation of propargyl compounds. Data published before 1971 are considered in those cases where this is necessary for the purposes of exposition.

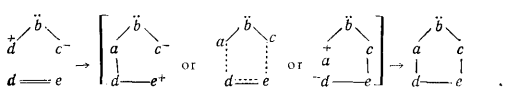
II. CYCLOADDITION

The cyclisation reactions of unsaturated systems in which rings are formed solely as a result of the rupture of π-bonds without the elimination of any fragment are known as cycloaddition reactions. These reactions constitute a universal method for the synthesis of various carbocyclic and heterocyclic systems. They include, for example, the widely familiar carbene and diene syntheses, 1,3-dipolar cycloaddition, and [2 + 2]cycloaddition.

Cycloaddition reactions with participation of ethynyl compounds have been most fully examined in a monograph[10].

1. 1,3-Dipolar Cycloaddition

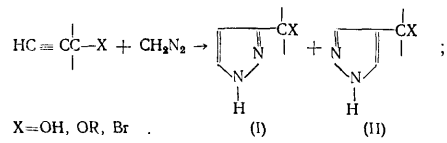
A clear-cut classification of 1,3-dipolar cycloadditions has been devised by Huisgen[17]. According to Huisgen's definition, any compound *a*–*b*–*c*, in which the atom *a* has an electron sextet and is a positive centre, the atom *c* has a free electron pair and carries a negative charge, and the atom *b* usually possesses an unshared electron pair, can constitute a 1,3-dipolar system. Problems of the mechanism of the 1,3-cycloaddition have been frequently discussed in the literature[18-20] and can be represented in a general form as follows:



Diazoalkanes, azides, nitrile ylides, nitrile imines, and nitrile oxides are typical 1,3-dipoles.

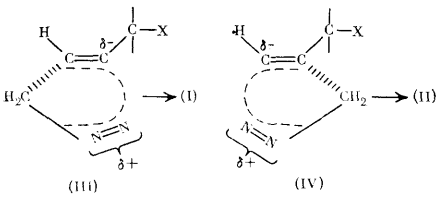
(a) Cycloaddition of Diazoalkanes

When propargyl compounds interact with diazoalkanes, substituted pyrazoles are formed. Thus the cycloaddition of diazomethane to propargyl alcohols, propargyl ethers, or propargyl bromides leads to two pyrazole isomers[21-23]:



X=OH, OR, Br . (I) (II)

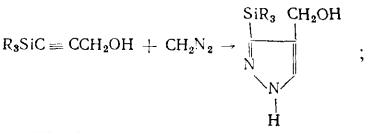
The ratio of the isomers depends on the nature of the substituents. Thus in the case of methylphenylethynylmethanol mainly the isomer (II) is formed; on the other hand, the main product of the reaction of propargyl bromide is the isomer (I). The reaction apparently proceeds via the transition states (III) and (IV):



(III) (IV)

It has been established[24] that the mode of 1,3-cycloaddition of substituted propargyl compounds to diazomethane is independent of the steric effect of the substituents and the electrostatic effects and that the decisive factor is the nucleophilic and electrophilic properties of the atoms between which a bond is formed.

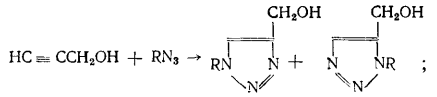
Pyrazoles are also produced in the interaction of propargyl compounds with substituted diazoalkanes. Propargyl alcohols and propargyl ethers react with methyl- or dialkyl-diazomethanes[21,25] to form exclusively an isomer of type (I), while an isomer of type (II) is obtained only from phenyl-substituted propargyl alcohols and ethers. Similar pyrazoles are also formed in the interaction of trifluorodiazoethane with propargyl bromide[26]. C_{sp}-trimethyl- or triphenylsilyl-substituted propargyl alcohols[27,28] are capable of entering into this reaction, an isomer of type (II) being mainly formed:



R=CH_3, C_6H_5 .

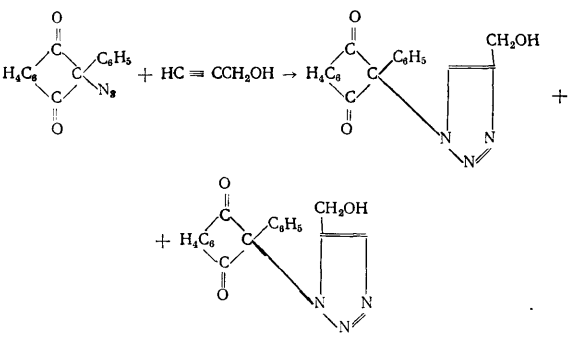
(b) Cycloaddition of Azides

The cycloaddition of azides to propargyl compounds leads to the corresponding triazoles, for example[29]:

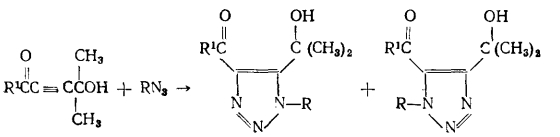


R=C_6H_5, $C_6H_5CH_2$.

2-(4-Hydroxymethyl-1,2,3-triazol-1-yl)- and 2-(5-hydroxymethyl-1,2,3-triazol-1-yl)-2-phenylindan-1,3-diones are formed from 2-azido-2-phenylindan-1,3-dione and propargyl alcohol[30]:



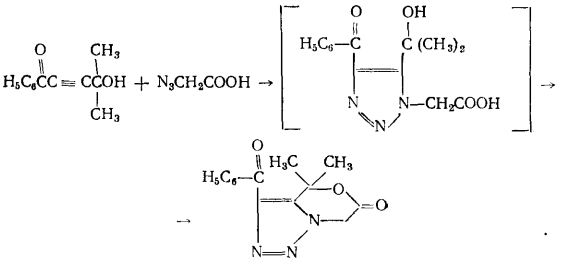
The ease of the cycloaddition of azides to propargyl compounds depends on the nature of the substituent at the triple bond and the structure of the azide. C_{sp}-bromo-substituted propargyl alcohols are less reactive than the unsubstituted alcohols[31]. Tertiary propargyl alcohols react with benzyl azide to form triazoles more readily than in the reaction with phenyl azide. The reactions of organic azides with the Iotsich reagent, obtained from propargyl alcohol, do not lead to cyclic compounds[32]. C_{sp}-acyl-substituted propargyl alcohols can also enter into the 1,3-cycloaddition reaction[33]:



Here the main factor determining the direction of the reaction is the high polarisation of the conjugated ketoethynyl system, which is responsible for the preferential formation of 1-R-4-acyl-substituted 1,2,3-triazoles. However, when aryl azides are introduced into the reaction, such regioselectivity is not observed. The ratio of the 4- and 5-acyl-substituted isomers changes in this instance towards an increase in the content of the latter.

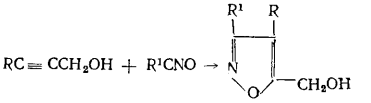
It is noteworthy that electron-donating (alkyl) substituents in the azide facilitate cycloaddition while electron-accepting substituents hinder it.

In certain cases the cycloaddition of azides to C_{sp}-acyl-substituted propargyl alcohol is accompanied by secondary processes involving the functional groups of the azide and the propargyl component. Thus azidoacetic acid reacts with benzoylethynyldimethylmethanol to form 4-benzoyl-1-methoxycarbonyl-5-(1-hydroxy-1-methylethyl)-1,2,3-triazole, which readily undergoes lactonisation:

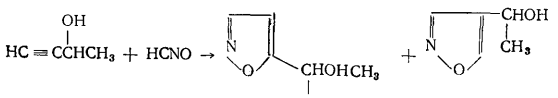


(c) Cycloaddition of Nitrile *N*-oxides

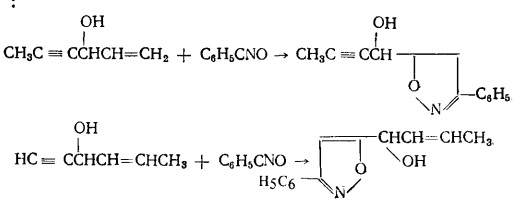
Propargyl alcohols readily react with nitrile oxides to form isoxazole derivatives[34,35]:



Secondary propargyl alcohols give rise to a mixture of isomeric isoxazoles[36]:



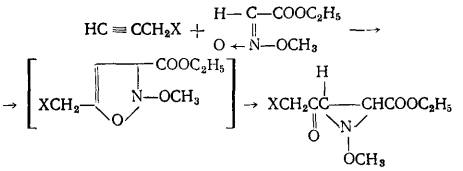
When benzonitrile oxide interacts with secondary vinylpropargyl alcohols, the addition can involve the double or triple bond depending on the structure of the initial compound[37]:



The 1,3-cycloaddition of nitrile oxides to propargylamines also leads to isoxazole derivatives[38].

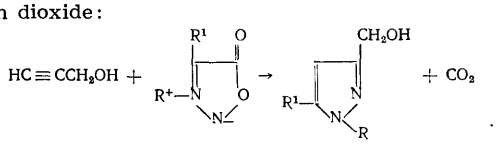
The mechanism of the formation of isoxazoles has been determined from the amount of incorporated deuterium[39]. It has been suggested that isomeric isoxazoles are obtained either directly via 1,3-dipolar cycloaddition or via the intermediate formation of the oxime $RC(=NOH)C\equiv CR^1$ with subsequent cyclisation. In the presence of D_2O isoxazoles free of deuterium are formed in the former case and [4-D]-isoxazoles are the products in the latter case.

Aziridine derivatives are formed in the reaction of propargyl alcohol and propargyl chloride with nitronic ester[40]. This is apparently associated with the rearrangement of the substituted 4-isoxazoline obtained in the first stage of the reaction:

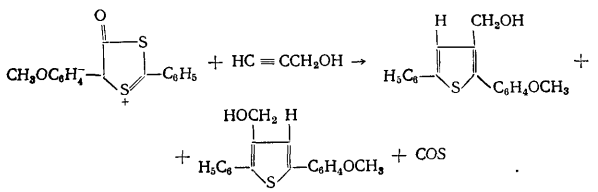


(d) Other Cycloaddition Reactions

Mesoionic compounds can also be regarded as 1,3-dipoles. They can form five-membered rings on reaction with propargyl compounds. Thus the interaction of 3-R-4-R^1-sydnone with propargyl alcohol leads to the formation of a pyrazole derivative[41]. Here the sydnone reacts via a [3 + 2]cycloaddition mechanism with simultaneous elimination of carbon dioxide:



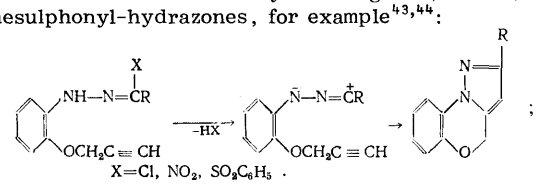
In the cycloaddition of mesoionic 1,3-dithiolones to propargyl alcohol, carbonyl sulphide is split off and a mixture of isomeric thiophens is formed[42]:



(e) Intramolecular Cycloadditions

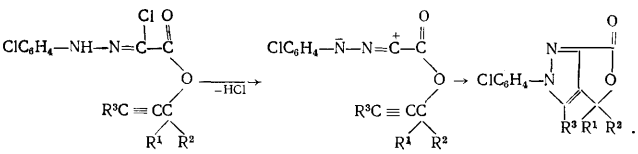
The reaction involving cycloaddition to propargyl compounds can occur not only intermolecularly but also intramolecularly. Such reactions involve molecules containing the necessary functional groups[17] (in a particular instance a 1,3-dipolar and a propargyl fragment).

The intramolecular cycloaddition of propargyl-substituted nitrile imines leads to the corresponding condensed pyrazoles. The sources of nitrile imines may be halogeno-, nitro-, and benzenesulphonyl-hydrazones, for example[43,44]:



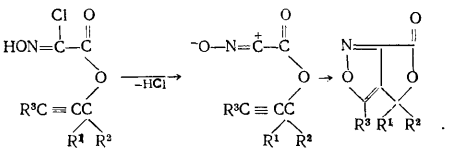
The ease of ring closure depends on the nature of the substituent R in the nitrile imine residue. In the case of the CH_2OH group, cyclisation does not occur.

The elimination of hydrogen chloride from "propargyl oxalate chlorohydrazone" leads to the formation of nitrile imines in which there is a possibility of intramolecular cycloaddition[45]. This results in the formation of furopyrazole derivatives:

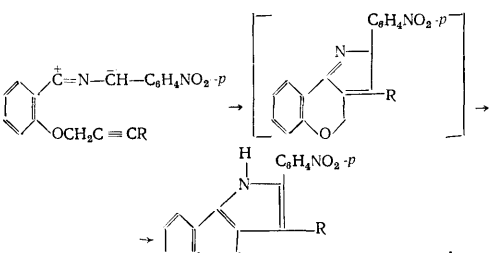


An analogous behaviour has been observed for "propargyl oxamide chlorohydrazone" but here the product is a mixture of isomeric pyrazoles[46].

Nitrile oxides with a propargyl fragment also readily undergo intramolecular cycloaddition. When "propargyl oxalate chloro-oximes" are heated in benzene in the presence of triethylamine, isoxazole derivatives are formed[45]:

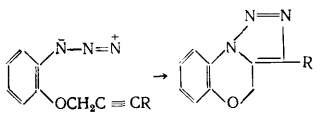


Benzopyranoisoxazole has been synthesised analogously[47]. It is noteworthy that the first reaction is structurally selective—only traces of the second isomeric adduct are formed, while both isomers are produced in the last reaction. Propargyl-substituted nitrile ylides are converted into benzopyranopyrrole derivatives as a result of intramolecular cycloaddition[48]:

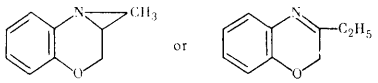


C_{sp}-Phenyl-substituted propargyloxy-derivatives give rise to pyrrole in a low yield (6%) under these conditions, which can be accounted for by the steric hindrance due to the C_6H_5 group.

Aryl azides containing the propargyloxy-group are converted into triazolobenzoxazines on intramolecular cycloaddition[49]:

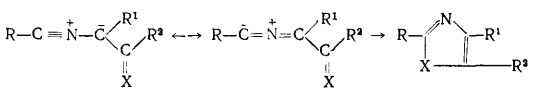


This is the first example of the intramolecular cycloaddition of the azide group to a triple bond. It is noteworthy that, in contrast to propargyl-substituted azides, azides with allyl groups form unstable Δ^2-1,2,3-triazolines, whose subsequent decomposition with elimination of molecular nitrogen gives rise to the reaction product:



2-Propargylthiophenyl azide undergoes analogous heterocyclisation to triazolobenzothiazine.

The intramolecular cycloaddition of nitrogen-containing analogues of propargyl-allenyl dipoles via the mechanism

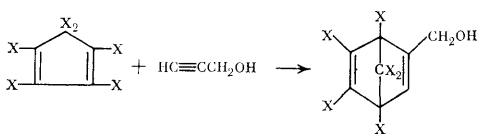


is of considerable interest. These reactions have already been surveyed and examined in a review[51].

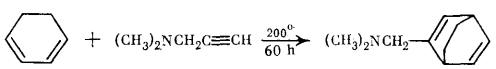
2. The Diene Synthesis

The Diels–Alder reaction belongs to the class of thermally allowed concerted processes[52], which means that unexcited molecules having 4π and 2π electrons respectively are combined. The diene synthesis has been discussed in detail in monographs[10,53,54] and in a review[19].

Propargyl compounds are active dienophiles. Thus propargyl alcohol reacts with hexachlorocyclopentadiene[55–57] and cyclopentadiene[58] at 130–150 °C to form the corresponding bicycloheptadienes:

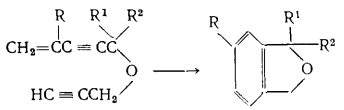


Propargyl chloroacetates[59,60] as well as the propargyl esters of trihalogenoacetic acids[61] react with the above dienes under analogous conditions. The yield of the adducts of the propargyl esters of trihalogenoacetic acids with hexachlorocyclopentadiene increases with increase of the atomic number of the halogen, while the opposite behaviour is observed for the adducts with cyclopentadiene. The reaction of dimethylpropargylamine with cyclohexadiene leads to cyclisation products in accordance with the mechanism[62]:

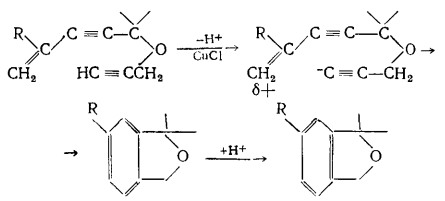


The reaction with the amine hydrochloride proceeds analogously. Allyldimethylamine does not react with cyclohexadiene under these conditions.

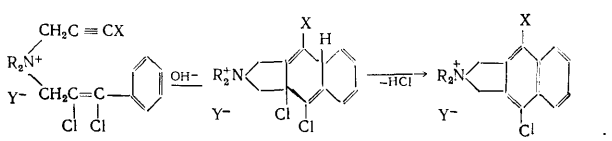
Propargyl compounds in which both reaction centres are located in the same molecule also enter into the diene synthesis. Thus intramolecular cyclisation with formation of phthalanes takes place on heat treatment of the propargyl ethers of vinyl- and isopropenyl-acetylenic alcohols[63]:



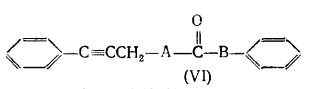
C_{sp}-Substituted propargyl ethers of vinylacetylenic alcohols also cyclise under analogous conditions[64]. The nature of the substituent in the acetylenic group has a significant influence on the reaction[65]. Electron-accepting groups facilitate cyclisation, while electron-donating groups greatly hinder it. Copper chloride has been used as a catalyst in order to accelerate the diene concentration[66]. The role of the catalyst apparently consists in the formation of the ethynyl carbanion:



It is noteworthy that the intramolecular condensation of the propargyl ethers of phenylacetylenic alcohols proceeds under more severe conditions than that of their vinylacetylenic analogues[67]. The diene synthesis involving β,γ-dichloro-γ-phenylallyl(propargyl)ammonium halide salts in the presence of alkalis proceeds with elimination of HCl and leads to benzoindolinium derivatives in high yields[68]:



Alkenylphenylallylammonium salts undergo the diene condensation also in the absence of alkalis. The intramolecular 1,4-cycloaddition of propargyl compounds of type (VI) in the presence of acetic anhydride opens a new pathway to synthetic lignan lactones[69–72]:

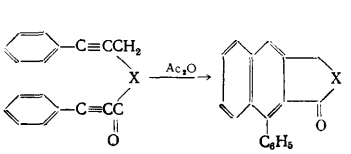


(VI)

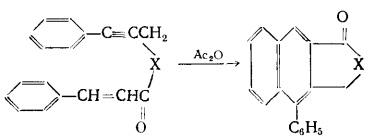
A=O, NH, $NCH_2C_6H_5$

B= *cis*-CH=CH, *trans*-CH=CH, C≡C .

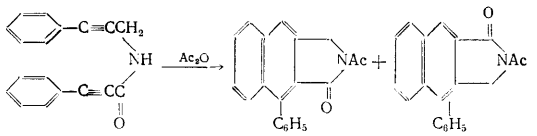
Here there is a possibility of the following pathways in the 1,4-cycloaddition: (1) electron-donating dienes interact with electron-accepting dienophiles (normal reaction); (2) electron-accepting dienes interact with electron-donating dienophiles (anomalous reaction). In the reaction of *N*-benzyldiynamide[70] and a diyne ester[69] the first pathway operates:



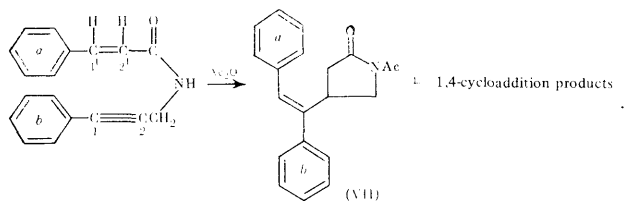
The intramolecular cycloaddition of *cis*- and *trans*-enynamides[71] and also of *N*-benzyl-*trans*-enynamide[70] proceeds via the second pathway:



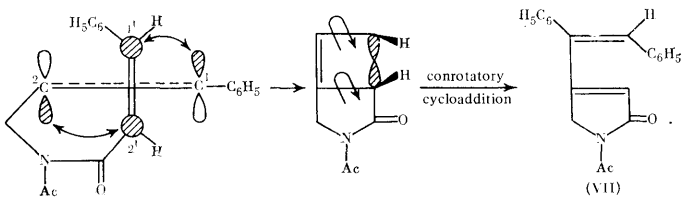
In the case of diynamides both pathways operate[71]:



There exist data[72] showing that, together with 1,4-cycloaddition products, yet another compound [compound (VII)] is formed in the intramolecular condensation of N-phenylpropargylamide of *cis*-cinnamic acid in the presence of acetic anhydride:

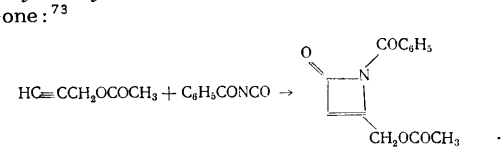


The use of deutero- and bromo-substituted analogues shows that compound (VII) is obtained as a result of the total rupture of the bond between the C(1′) and C(2′) atoms with formation of new C(1)–C(1′) and C(2)–C(2′) bonds. It has been suggested that this reaction takes place as a result of the thermally induced intramolecular concerted $[{}_{\pi}2_{s} + {}_{\pi}2_{a}]$-cycloaddition with formation of the sterically strained cyclobutene and subsequent conrotatory cyclodecomposition of the cyclobutene via the $[{}_{\sigma}2_{a} + {}_{\pi}2_{s}]$- or $[{}_{\sigma}2_{s} + {}_{\pi}2_{a}]$-mechanism. New bonds are formed in the suprafacial addition to the *cis*-C=C bond and the antarafacial addition to the C≡C bond. These bonds exhibit electron-donating and electron-accepting properties respectively:



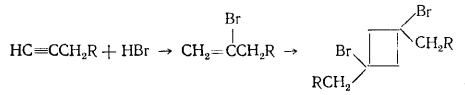
3. 1,2-Cycloaddition

The 1,2-cycloaddition to propargyl compounds has been studied inadequately. The interaction of propargyl acetate with benzoyl isocyanates leads to a substituted 1-benzoyl-2-azetin-4-one:[73]



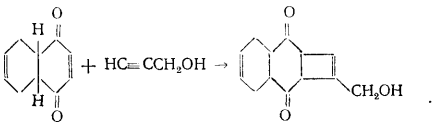
The cycloaddition of methyl propargyl ether to trichloroacetyl and benzoyl isocyanate has been considered in reviews[74,75].

The formation of cyclobutane derivatives from compounds of the type $HC{\equiv}CCH_2R$ in the presence of anhydrous HBr has been observed recently[76]. Together with the usual addition products, *cis*- and *trans*-1,3-dialkyl-1,3-dibromocyclobutanes are formed under these conditions (as a result of cyclodimerisation):



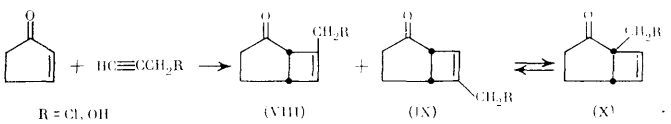
By varying the reaction conditions and the substituents R, it is possible to obtain cycloaddition products with maximum yields.

The photocycloaddition of a Δ^2-ene-1,4-dione to propargyl alcohol ($\lambda > 300$ nm) in benzene at room temperature leads to adducts of the tricyclo[6.4.0.0^{3,6}]dodecane series containing the cyclobutene ring[77]:



Under the same conditions, cyclopent-2-ene-1,4-diones do not form such rings owing to their extremely high tendency towards photopolymerisation. However, by altering the reaction conditions, it is possible to achieve the cycloaddition of propargyl alcohol in this case also[77].

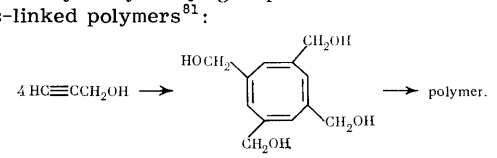
In order to elucidate the influence of the nature of the substituent in propargyl compounds on the ease and structural specificity of the cycloaddition, the photocycloaddition of cyclopent-2-en-1-one to propargyl chloride and propargyl alcohol has been investigated[78,79]:



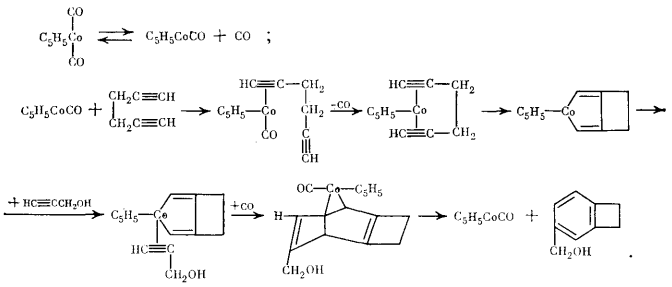
The reaction of cyclopentenone with propargyl chloride in ether proceeds comparatively unambiguously. Only the "head-to-head" and "head-to-tail" adducts, compounds (VIII) and (IX) respectively, are formed at the beginning of the photolysis in proportions of 3:1, after which their photoisomerisation products (X) appear. At the end of the photolysis the product of the addition of the solvent to cyclopentenone also accumulates. The reaction of propargyl alcohol with cyclopentenone in benzene is slow and compounds (VIII) and (IX) obtained initially undergo photopolymerisation with formation of minor products having a labile structure. It has been established that the structural specificity of the cycloaddition of cyclopentenone to propargyl compounds depends greatly on steric factors.

Methoxymethyl-3,4-carbonyldioxycyclobutene is formed in 22% yield in the photocycloaddition of methyl propargyl ether to vinylene carbonate[75].

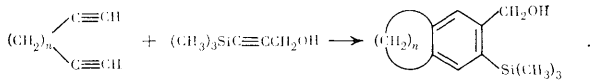
The cyclodimerisation, cyclotrimerisation, and cyclooligomerisation reactions also belong to the class of 1,2-cycloadditions. The direction of these reactions depends mainly on the type of catalyst employed. Thus cyclic trimers and tetramers have been synthesised from propargyl alcohols in the presence of di(π-allyl)nickel[80]. The cyclisation of propargyl alcohol catalysed by nickel acetylacetonate and its mixture with triphenylphosphine leads to 1,3,5,7-tetra-(hydroxymethyl)cyclo-octatetraenes. When the latter are heated, the hydroxymethyl groups condense with formation of cross-linked polymers[81]:



The most active catalysts in the intermolecular cycloaddition of propargyl compounds are transition metals[82,83]. The 1,2-cycloaddition process has been thoroughly investigated in relation to the interaction of propargyl alcohol with bipropargyl and its C_{sp}-substituted derivatives in the presence of Δ^5-cyclopentadienylcobalt dicarbonyl[84]. The results obtained[85,86] led to many well-founded hypotheses concerning the reaction mechanism which reduces, to the following scheme[84]:



The reaction of silicon-containing propargyl compounds with diacetylenes catalysed by $C_5H_5Co(CO)_2$ is an interesting type of cocyclisation[87–89]:



An increase in the length of the polymethylene chain favours cycloaddition.

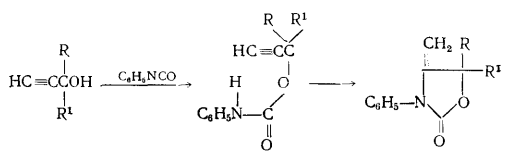
III. CYCLISATION

1. Intramolecular Addition to the Triple Bond

The cyclisation of propargyl compounds via intramolecular addition to the triple bond has found extensive applications in the synthesis of a wide variety of carbocyclic and heterocyclic systems. The rings are formed via the intramolecular addition of NH, OH, CH, SH, and ZH groups.

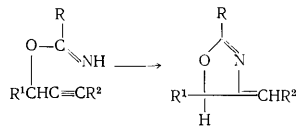
(a) NH-Addition

Five-membered heterocycles are synthesised by the intramolecular attack by the NH group on the C≡C bond. Thus the interaction of terminal propargyl alcohols with phenyl isocyanate leads initially to the corresponding carbamates, which readily undergo intramolecular cyclisation in the presence of bases and are converted into oxazolidinones[90–93]:



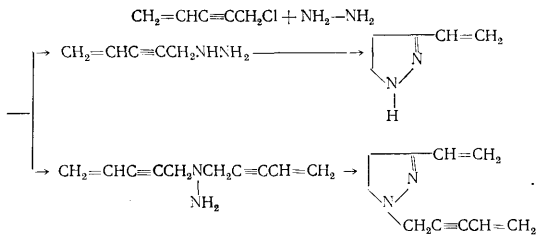
When the acetylenic hydrogen atom in the initial alcohol is replaced by bromine, bromo-oxazolidinones are formed, but, when the hydrogen is replaced by the aminomethyl group, the reaction cannot be carried out[93]. This difference in the behaviour of the aminoalcohol carbamates and their analogues can be explained by the polar influence of the C_{sp} substituent. Since heterocyclisation takes place as a result of the nucleophilic attack by the nitrogen atom of the carbamate group on the ethynyl carbon atom, the polarisation of the triple bond, generating a partial positive charge on the attacking atom, is essential for its successful occurrence.

On heating in benzene in the presence of 1,5-diazabicyclo-[5.4.0]undec-5-ene, propargyl benzimidates are converted into methyleneoxazolines in 45–50% yield[7]:

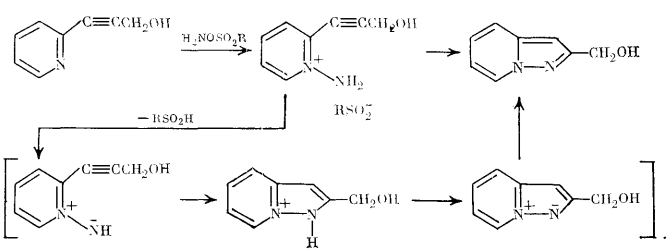


The latter are stable compounds. On treatment with t-C_4H_9OK, they are converted into oxazoles. The possibility of synthesising oxazole derivatives in the presence of Ag^+ or Hg^+ salts in 97.3% yield has been demonstrated recently[94].

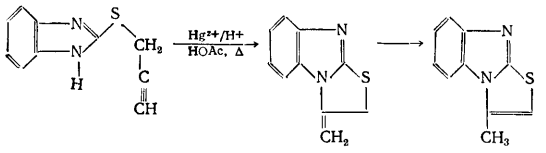
When hydrazine or phenylhydrazine reacts with primary vinylpropargyl halides in the presence of CuCl, substitution products are formed and then cyclise to vinylpyrazolines[95–98]:



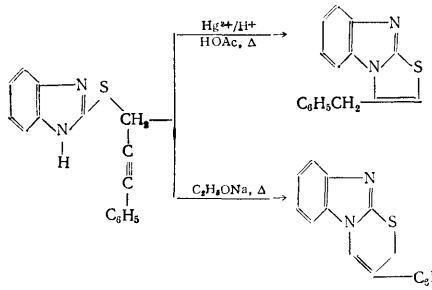
Tertiary vinylpropargyl halides and propargyl halides behave analogously in reactions with hydrazine. However, secondary vinylpropargyl halides do not give rise to pyrazolines, which are formed as a result of the direct attack by the nucleophile on the carbon atom linked to the halogen and subsequent cyclisation of the hydrazine formed. C_{sp}-pyridylpropargyl alcohol reacts with *O*-mesitylenesulphonylhydroxylamine to form the corresponding salt which is converted into pyrazolopyridine in 70–90% yield on treatment with potassium carbonate in dimethylformamide (DMF).[99] The similar transformation of propargylammonium compounds of the type $\diagdown\overset{+}{N}-CH_2C\equiv CH$ usually proceeds via a 2,3-sigmatropic rearrangement[100–102]. The explanation of the conversion of C_{sp}-pyridylpropargyl alcohol into pyrazolopyridine in terms of the formation of an allene intermediate is unconvincing, since it is difficult to assume the possibility of the formation of a strained five-membered cyclic compound with an allene group. It has been suggested[99] that the attack by NH on the electrophilic centre of the triple bond results in the formation of a dipolar ion which is stabilised as a consequence of the migration of hydrogen:



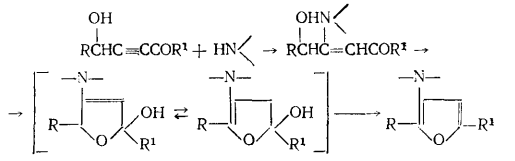
Terminal propargylthiobenzimidazoles give rise to satisfactory yields of 3-methylthiazolo[3,2-*a*]benzimidazoles in the presence of mercury ions[103]:



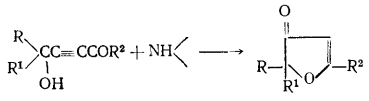
The cyclisation of C_{sp}-substituted propargylthiobenzimidazoles gives rise to 3-benzylthiazolo[3,2-*a*]benzimidazoles or 4-phenyldihydrothiazino[3,2-*a*]benzimidazoles depending on the reaction conditions[103]:



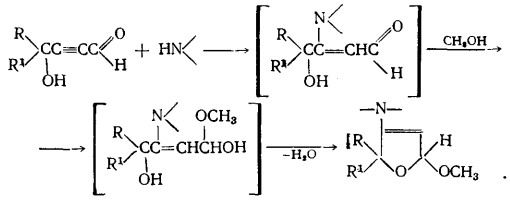
Certain reactions involving the addition of amines to propargyl compounds are accompanied by cyclisation. Thus the interaction of secondary propargyl ketols with primary and secondary amines leads to the formation of β-aminofurans[104,105]:



It has been suggested that nucleophilic addition of the amine to the triple bond takes place initially with subsequent cyclisation of the resulting aminovinylketol to β-aminofuran. Tertiary γ-ketols are converted into β-furanones on treatment with secondary amines and subsequent hydrolysis[106]:

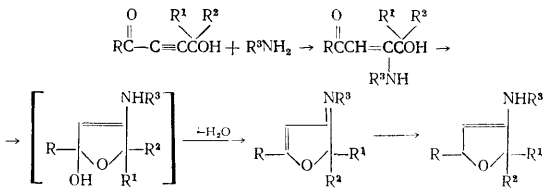


Propargylaldols react with primary amines to form acyclic compounds[107]. The attempts to achieve the nucleophilic addition of diethylamine to propargylketols in anhydrous media [ether, tetrahydrofuran (THF), and benzene] lead to tarry products[108]. Propargylaldols combine with dialkylamines in anhydrous methanol and are converted into stable 4-dialkylamino-2-methoxydihydrofurans in 43–54% yield. The solvent as well as the dialkylamine apparently adds on in this instance[108]:

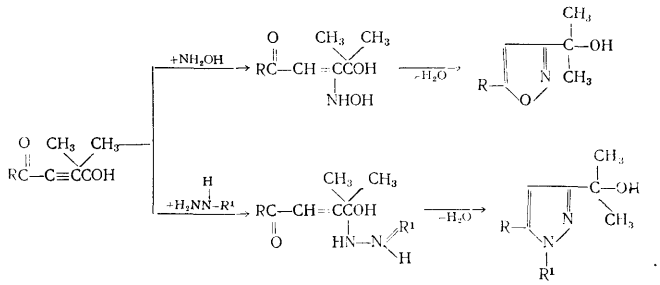


In absolute benzene or ether in an argon atmosphere the addition of diethylamine is accompanied by charring and an individual product cannot be isolated.

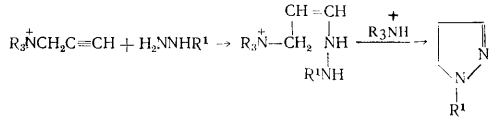
The addition of primary amines to propargylketols proceeds in accordance with the mechanism[109]:



The interaction of propargylketols with bifunctional nucleophiles (hydrazine, hydroxylamine) in a weakly alkaline medium involves the triple bond. The adducts formed initially cyclise to isoxazoles and pyrazoles[110]:

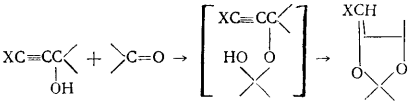


The reaction of hydrazine with trialkylpropargylammonium salts leads to the formation of pyrazolines[111]:



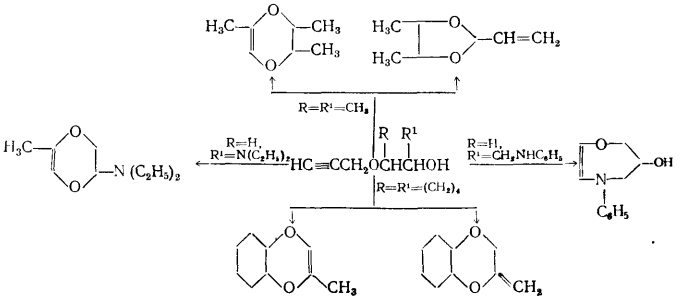
(b) OH-Addition

Among intramolecular cyclisations, the intramolecular addition of the OH group is of special interest. Thus it has been shown that, when propargyl alcohols interact with carbonyl compounds, substituted 1,3-dioxolans are formed[112–118]:

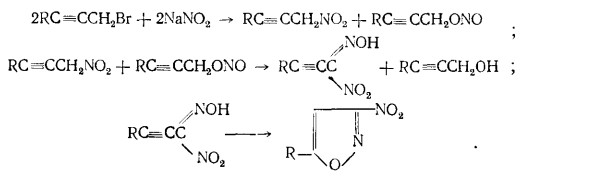


The extent and ease of cyclisation depend on the substituent X. The reaction proceeds readily when X = RC≡C, Br, RCOO, CN, or ROO.[117] On the other hand, the reaction does not occur at all when X = H, CH_2 = CH, C_6H_5O, CH_2OH, $CH(OC_2H_5)_2$, or CH_2OCH_3.[117,118] By comparing the spectroscopic characteristics of propargyl alcohols with their reactivities in the heterocyclisation reactions with carbonyl compounds, it has been established[117] that there is a qualitative relation between the reactivities of propargyl alcohols and the differences Δδ between the chemical shifts of the ≡CH group in the ^{1}H NMR spectra. Thus compounds for which Δδ is small are unreactive. Propargyl alcohols with functional group substituents which are actively involved in cyclisation have high values of Δδ.

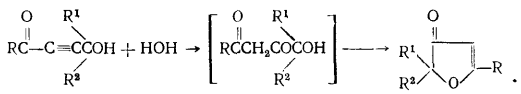
The cyclisation of alkyl-substituted propargyloxyethanols leads to rings of different size[119]:



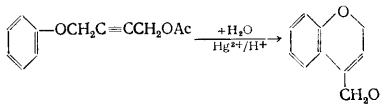
The application of propargyl compounds in the synthesis of isoxazole derivatives has been described[120]. Thus 3-nitroisoxazole has been obtained from propargyl bromide and sodium nitrite in DMF. The cyclisation of C_{sp}-substituted propargyl bromides also leads to 3-nitroisoxazoles[121]:



This mechanism has been confirmed by the isolation from the reaction mixture of a C_{sp}-substituted propargyl alcohol. In some cases the hydration of propargyl compounds also leads to the formation of rings. Propargylketols are fairly readily hydrated in dilute sulphuric acid or in alcoholic alkali in the presence of mercury salts and also in the presence of amines in protic solvents[104,122,123], being converted under these conditions into β-furanones, apparently via a β-diketol stage. In aqueous dioxan the yield of furanones is ≤50%:



Under analogous conditions, the C_{sp}-acetoxymethylpropargyl ether of phenol gives rise to 4-acetoxymethyl-Δ^3-chromene[124]:

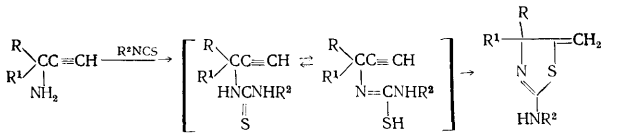


Under the same conditions, phenyl propargyl ether is converted into phenoxyacetone.

An interesting cyclisation of phenolic and enolic propargyl compounds has been discovered recently[125,126]. The monopropargyl ether of catechol is converted into 2,3-dihydro-2-methylene-1,4-benzodioxin in 65–90% yield on refluxing with mercury(II) oxide in DMF. In the absence of a catalyst and at temperatures below 110 °C, cyclisation does not occur. 2,3-Dihydro-2-methylenenaphtho[2,3-*b*]dioxin has been obtained under analogous conditions from the monopropargyl ether of 2,3-dihydroxynaphthalene.

(c) SH-Addition

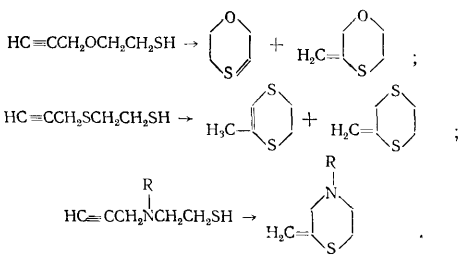
The intramolecular addition of the SH group to the C≡C bond is used to synthesise sulphur-containing heterocycles. There exists the view[127] that, when α,α-disubstituted propargylamines react with isothiocyanates, thiourea derivatives are formed initially and then give rise to the final reaction products under the influence of bases. However, Azerbaev et al.[128] believe that the intermediate thiourea derivatives are immediatley converted into thiazolines (via the thione–thiol tautomeric equilibrium):



Secondary α-propargylamines react with isothiocyanates to form thiazolidines. The reactions of isothiocyanates with secondary amines are slower than those with primary amines. It is noteworthy that cyclisation becomes more difficult with an increase in the bulk of the groups R^1 and R^2. The tendency towards cyclisation also diminishes with increase in the size of the group R. Similar features of the cyclisation had also been noted earlier[127,129] and the difficulties in the cyclisation reaction were accounted for by steric factors.

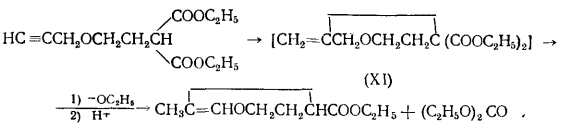
The interaction of α,α-disubstituted propargylamines with benzoyl isothiocyanate leads the formation of 2-benzamido-5-methylene-2-thiazoline[130]. It has recently been suggested[131] that the interaction of aryl isoselenocyanates with 2-alkynylamines proceeds analogously to the reaction with isothiocyanates, i.e. via the intermediate formation of seneloureas which undergo cyclisation during the reaction with formation of the corresponding selenazolines. The reactions of 2-propynylamines with isoselenocyanates proceed more vigorously than those with isothiocyanates.

Compounds containing heteroatoms between the thiol and propargyl groups can also be used to synthesise heterocycles. It has been established[132] that the structure of the products of the cyclisation of propargyl derivatives of hydroxy-, mercapto-, and amino-ethanethiols in the presence of bases depends on the nature of the heteroatom. Whereas a mixture of 2-methylene-1-thia-4-oxacyclohexane and 3-thia-6-oxacycloheptene is formed from propargyloxyethanethiol, in the reaction involving propargylthioethanethiol the main reaction products are 2-methylene-1,4-dithia-2-cyclohexene and 2-methylene-1,4-dithiacyclohexane. Only one cyclic product, namely 2-methylene-1-thia-4-azacyclohexane, is formed from propargylaminoethanethiol:



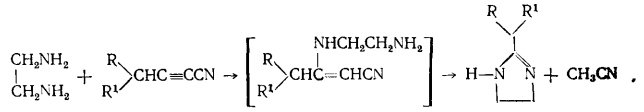
(d) CH-Addition

Propargyl compounds containing an active hydrogen atom undergo the Michael reaction with formation of cyclic compounds. Thus the intramolecular cyclisation of propargyloxyethylmalonic ester in the presence of sodium ethoxide in alcohol leads to derivatives of dihydropyran[133]:

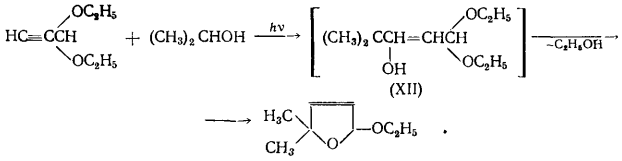


It has been suggested that the intermediate compound (XI) interacts with the ethoxide anion, splits off diethyl carbonate, and is converted into the final product.

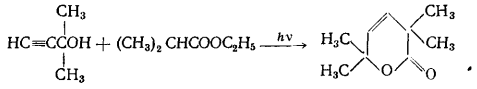
The Michael adducts of ethylenediamine and the "inverted" propargyl cyanides readily cyclise to imidazolines (yield 80%) with elimination of acetonitrile[134]:



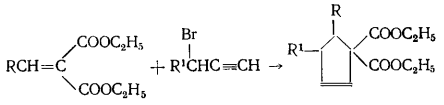
The photochemical reaction of the diethyl acetal of propiolaldehyde with isopropyl alcohol proceeds via the intermediate (XII) and gives rise to a dihydrofuran derivative as a result of the elimination of ethanol[135]:



Under these conditions, propargyl alcohols are converted into acyclic compounds[136]. The interaction of ethynyldimethylmethanol with ethyl isobutyrate results in the formation of a pyrone derivative[137]:

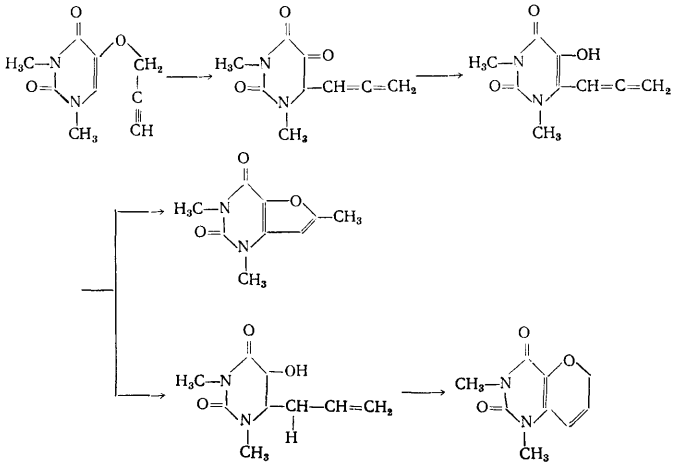


The addition of diethyl isobutylidenemalonate to secondary propargyl bromides in the presence of zinc or on heating in THF can be regarded as a new method of synthesis of cyclopentene derivatives[138]:

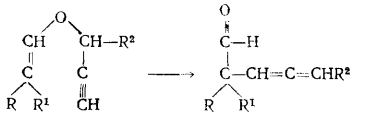


2. Cyclisation Involving the Claisen Rearrangement

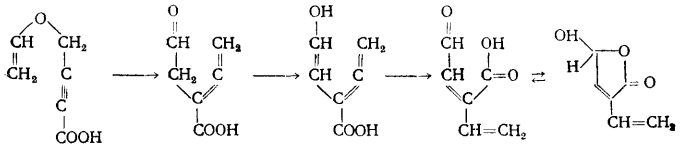
One of the commonest methods of synthesis of heterocycles involves the cyclisation of propargyl compounds via a sigmatropic rearrangement. Thus the thermal cyclisation of propargyl ethers of phenols leads to the formation of chromenes[75]. In contrast to this, the cyclisation of propargyloxyuracils results in the additional formation of furopyrimidine[2]:



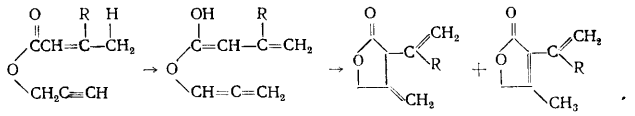
This can be explained by the fact that the electron-withdrawing effect of the uracil nucleus is greater than that of the phenyl group. This effect renders the central carbon atom of the allene fragment in the enol more electron deficient. As a consequence of this, the sensitivity of the enolic hydroxy-group to nucleophilic attack increases and ring closure results. The solvent exerts a decisive influence on the mode of cyclisation. Furopyrimidines (66%) are formed from substituted propargyloxyuracils in DMF at 130 °C. Pyrolysis in xylene at 130 °C leads to pyranopyrimidines (48%). The propargyl ethers of hydroxymethylacridone[4], substituted hydroxynapthalenes[3], coumarins[139–141], and hydroquinone[142] behave analogously in the intramolecular cyclisation reaction. Propargyl vinyl ethers react differently. Their thermal cyclisation with a vinyl fragment containing vinyl substituents leads to allenyl-substituted aldehydes[143]:



The cyclisation of the C_{sp}-carboxyether leads to the formation of a natural antibiotic—the lactone of dihydroxyvinylbutanoic acid[5]:

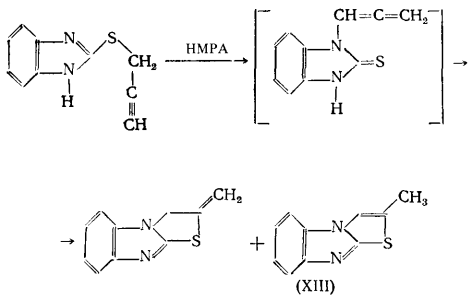


It has been suggested that the initial propargyl vinyl ether is converted via a cyclic transition state into an allene aldehyde, which undergoes a prototropic rearrangement with formation of a diene aldehyde which then cyclises to the final product. Alkenyl-γ-lactams and alkenyl-γ-lactones have been obtained from propargylamides or propargyl esters of alkanoic acids[144–146]. The reaction mechanism is as follows:

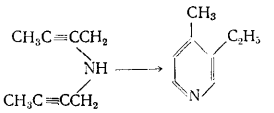


The unsaturated ester of the propargyl alcohol probably enolises with participation of an α-hydrogen atom as a result of 1,5-migration with formation of an intermediate, which is converted into the final product via the mechanism of the ene reaction involving the transfer of a hydrogen atom from the enol group.

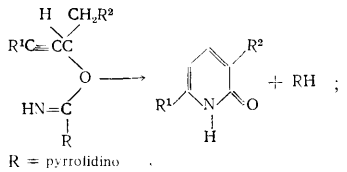
An instant rearrangement has been observed in the thermal cyclisation of propargylthiobenzimidazole in hexamethylphosphoramide (HMPA):[147,148]



Only compound (XIII) is formed in ethanol in the presence of sodium ethoxide. Under these conditions, dipropargyl sulphides do not cyclise. The thermal rearrangement of C_{sp}-alkyl-substituted dipropargylamines in the presence of potassium t-butoxide in butyl alcohol leads to alkylpyridines[149]:



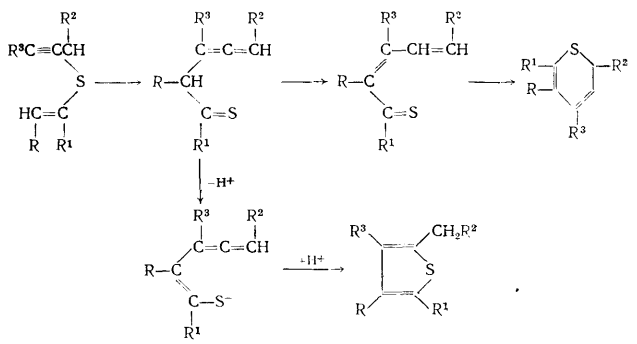
Under these conditions, the unsubstituted dipropargylamine is converted into the corresponding nitrile. A new method of synthesis of 2-pyridones by the thermolysis of *O*-propargyl derivatives of isoureas has been described[150,151]:



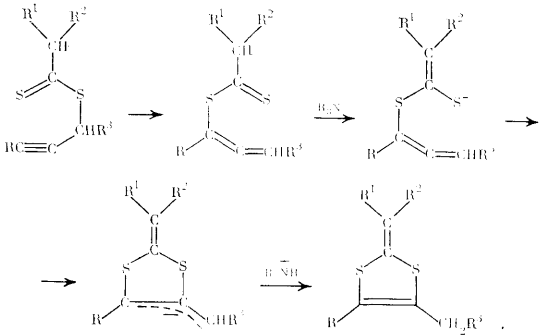
R = pyrrolidino .

It has been suggested that the initial reaction stage is the thermal 3,3-sigmatropic rearrangement of the initial compound into an allene, whose tautomeric transformation gives rise to the corresponding diene. The elimination of pyrrolidine from the diene leads subsequently to an isocyanatodiene, which undergoes electrocyclic cyclisation to a pyridone.

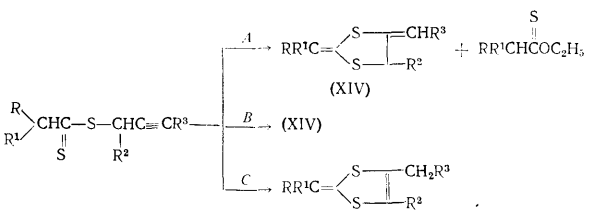
Sulphur-containing vinylpropargyl compounds also undergo the Claisen rearrangement[152,153]. An allene intermediate is formed in the initial stage. Its subsequent transformation can take place with formation of various substituted heterocycles:



The solvent and the presence of an amine exert the most significant influence on the direction of the reaction. The reaction in HMPA leads to the specific synthesis of 2*H*-thiopyrans. The basicity of HMPA apparently favours the 1,3-isomerisation of the allene intermediate to a conjugated diene, whose subsequent transformation leads to a thiopyran. When the reaction is carried out in HMPA or dimethyl sulphoxide (DMSO) in the presence of amines, mixtures of substituted thiopyrans and thiophens are formed. Amines probably catalyse the conversion of the allene intermediate into a thiophen. Propargyl vinyl sulphides containing the cyano-group in the vinyl fragment gives rise to thiopyrans on heating in silicone oil, while in DMSO in the presence of di-isopropylamine they produce a mixture of thiopyran and thiophens[154]. Propargylthiothiopyran cyclises like propargyl sulphides with formation of thiopyranothiopyran and thiopyranothiophen[155]. The thermal cyclisation of propargyl alkanedithioates in xylene proceeds via the mechanism[156]



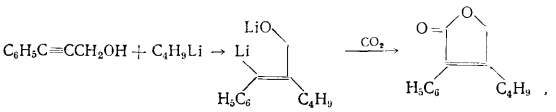
The base-catalysed cyclisation of propargyl alkanedithioates has been investigated[157]. The reaction can be carried out in the presence of sodium ethoxide in absolute alcohol (method *A*) or in the presence of potassium t-butoxide in a mixture of t-butyl alcohol and the dimethyl ether of ethylene glycol (method *B*) and also in the presence of sodium ethoxide or potassium t-butoxide in the dry dimethyl ether of ethylene glycol (method *C*):



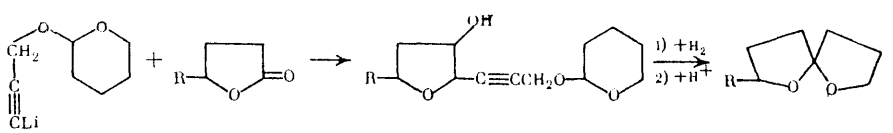
3. Other Cyclisation Reactions

Apart from the reactions described, a number of non-general cyclisation reactions have been described for propargyl compounds.

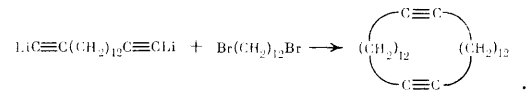
C_{sp}-phenyl-substituted propargyl alcohol readily reacts with butyl-lithium in ether in the presence of symmetrical *N*,*N*'-dimethylethylenediamine to form an intermediate whose reaction with carbon dioxide leads to the corresponding lactone in a yield up to 70%:[158]



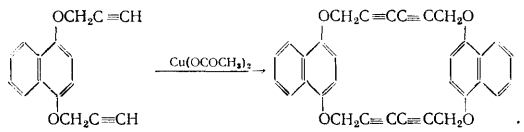
C_{sp}-Lithio-derivatives of propargyl ethers react with lactones in diethyl ether and give rise to hydroxylactones whose hydrogenation and subsequent acid hydrolysis afford the corresponding spiro-compounds[159]:



The dilithio-derivative of hexadeca-1,10-diyne is readily alkylated by 1,12-dibromododecane in a THF–HMPA mixture with formation of a 28-membered macrocycloalkadiyne[160]:

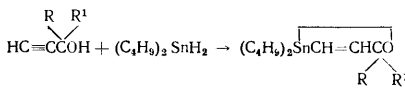


The intermolecular cyclisation of 1,4-dipropargyloxynaphthalene in the presence of copper acetate on heating in pyridine has been reported recently[161]. The reaction leads to the formation of a tetrayne crown-ether in 96% yield:



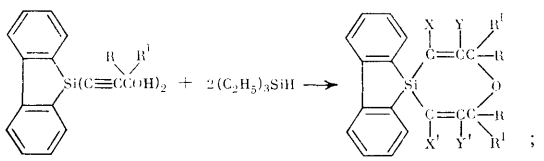
Other propargyl ethers have also been introduced into this reaction[162].

The interaction of dibutylstannane with propargyl alcohols leads to unsaturated cyclic organotin ethers[163]:



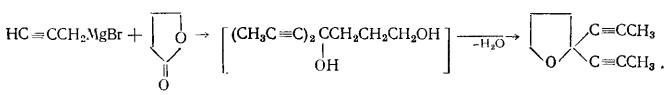
The addition of dialkylchlorohydrosilanes and the corresponding germanes and stannanes to substituted propargyl alcohols gives rise to the corresponding γ-hydroxyalkenyl analogues. The reduction of the latter with lithium tetrahydroaluminate and subsequent intramolecular dehydrocondensation led to the synthesis of 2-sila-, 2-germa, and 2-stanna-1-oxacyclopentanes[164]. The ease of cyclisation depends on the polarity of the metal–hydrogen bond.

Iotsich reagents derived from propargyl alcohols react with dichlorosilafluorene to form silicon-containing glycols whose hydrosilylation with triethylsilane is accompanied by cyclodehydration[165]:

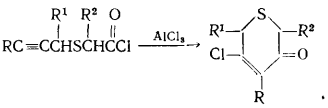


X, Y, X', Y' = $(C_2H_5)_3Si$ or H .

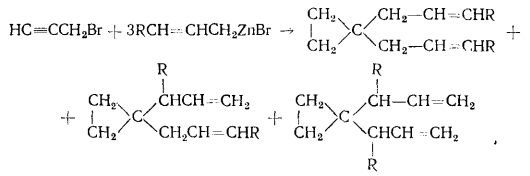
There exists the view that the final product of the interaction of the Grignard reagent derived from propargyl bromide with γ-butyrolactone, namely 2,2-dipropynyltetrahydrofuran, is also formed via the cyclodehydration of the intermediate 1,4-diol:[166]



The intramolecular cyclisation of chlorides of propargylthioalkanecarboxylic acids catalysed by $AlCl_3$ leads to derivatives of dihydrothiopyranones[167]:



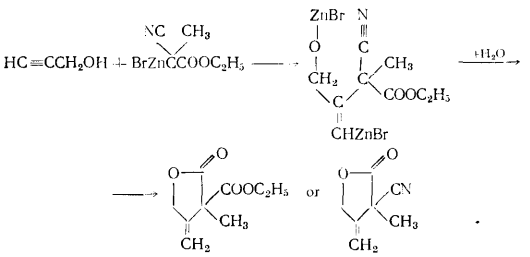
The addition of unsaturated organozinc compounds to the propargyl compounds $HC\equiv CCH_2X$ leads either to the normal adducts or to cyclic compounds[168–170]. The reactions of propargyl alcohols (X = OH), ethers (X = OR), and their nitrogen-containing analogues (X = NR_2) result in the formation of mono- or di-addition products. Only diaddition takes place in the reaction of propargyl bromide or chloride with subsequent 1,3-elimination and the formation of cyclopropane derivatives. When propargyl bromide is treated with substituted allyl derivatives of organozinc compounds, mixtures of three substituted cyclopropanes are produced:



The Iotsich reagent derived from phenyl propargyl ether reacts with C_{sp}-ethyl-substituted propargylzinc bromide, also forming a cyclopropane derivative[171]. In contrast to this, the formation of acyclic compounds is observed in the reaction of propargyl alcohol with the Iotsich reagent.

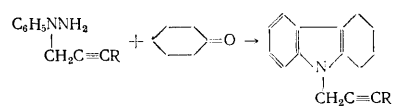
Treatment of propargyl bromide with organomagnesium compounds results in the formation of the products of the Wurtz exchange reaction and also the products of an intramolecular rearrangement[172–174].

The reaction of propargyl alcohol with the zinc derivative of ethyl bromocyanopropionate leads to the formation of γ-lactones[175,176]:

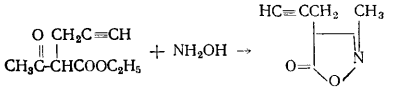


Mixtures consisting of lactones, adducts, and transesterification products are formed from secondary propargyl alcohols. The reaction involving tertiary propargyl alcohols affords a complex mixture of products Under these conditions, C_{sp}-substituted propargyl alcohols do not react and diethylpropargylamine gives rise to addition products alone.

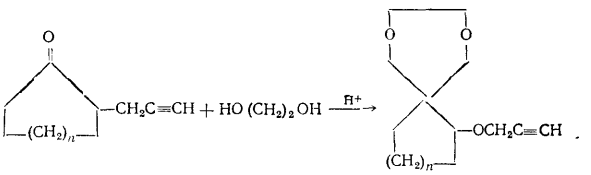
Certain cyclisation reactions of propargyl compounds proceed without involving the triple bond. This permits the specific use of the latter in subsequent reactions. Propargylphenylhydrazines are readily converted into *N*-propargyltetrahydrocarbazoles on interaction with cyclohexanone in acetic acid[177]:



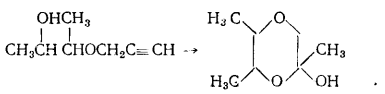
The propargyl group is retained also in the intermolecular cyclisation of ethyl propargylacetoacetate with hydroxylamine[178]:



2-Propargylcycloanones react with glycol to form the corresponding propargyl spirodioxolans[179]:



The monopropargyl ether of butane-2,3-diol undergoes cyclohydration in an aqueous medium in the presence of mercury(II) oxide and sulphuric acid with formation of 2-hydroxy-2,5,6-trimethyl-1,4-dioxan[180]:



The interaction of propargyl alcohols with the β-chloroalkyl ethers of glycidol in the presence of $BF_3.(C_2H_5)_2O$ leads to the formation of derivatives of propargyloxymethyl-1,4-dioxan[181].

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