Russian Chemical Reviews

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September 1960

VINYLACETYLENE AND ITS HOMOLOGUES

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INTRODUCTION

Vinylacetylene production is one of the main applications of acetylene in present-day industry. The prospects for increased production of vinylacetylene as well as of its homologues were recently greatly improved by the treatment of natural, petroleum and by-product gases. The possibilities for the utilisation of vinylacetylenic hydrocarbons in chemical industry are far from being exhausted, as is

borne out by the number of papers on enynes appearing in recent chemical literature.

Vinylacetylenic hydrocarbons are of considerable interest also for theoretical organic chemistry. Their polarity, high polarisability, and the characteristic rigidity of configuration bring out clearly the influence of structural factors on chemical reactivity.

The chemical literature contains no complete review of the methods of preparation or the properties of enyne hydrocarbons.

Enynes – hydrocarbons with two different types of multiple bonds, double and triple – were little known till about 1930. They began to attract attention after Nieuwland's discovery of the dimerisation of acetylene in the presence of cuprous chloride (1931)[1], which subsequently became a basis for the industrial preparation of chloroprene rubber.

The first enyne hydrocarbons to be prepared were hex-1-en-5-yne (1878)[2] and pent-1-en-3-yne, "perylene" (1882)[3], but the structure of the latter was not established till 1942[4-8]. The first member of the enyne series, vinylacetylene, was described in 1913 by Willstätter[9]. By 1931, besides the above-mentioned hydrocarbons, isopropenyl-[10], isobutenyl-[11], isopentenyl-[12], and allylacetylene[13] had also become known, as had some aromatic vinylacetylenes[14-16]. But the great majority of enyne hydrocarbons known at present, whose formulae and constants are given in Table 2, were first described within the last 20 years, namely after the discovery of the practical value of vinylacetylene.

I. METHODS FOR THE PREPARATION OF ENYNE HYDROCARBONS

Some vinylacetylenes occur in essential oils. For instance, the essential oil from *Agropyrum repens* and some other grasses contains the hydrocarbon "agropyrene" or "capillene", whose structure is apparently similar to, but not identical with, that of phenylpent-2-en-4-yne[17,19].

Enyne hydrocarbons can be prepared by a large number of synthetic methods, acetylene being the most widely used starting material. These are reviewed below in accordance with the nature of the chemical processes involved.

A. PREPARATION FROM COMPOUNDS WITH THE SAME NUMBER OF CARBON ATOMS

1. Preparation from Halogen Derivatives

Dehydrohalogenation of halogen derivatives is a classical method for the synthesis of a very wide range of unsaturated compounds, including the enyne hydrocarbons with conjugated and isolated multiple bonds.

Thus, a series of enyne hydrocarbons was prepared by one of the oldest methods – treatment with KOH of products from the reaction between unsaturated ketones and PCl_5, [2,7,8,20-22]:

$$CH_3-CO-CH_2-CH_2-CH=CH_2 \xrightarrow{PCl_5} CH_2=CCl-CH_2-CH_2-CH=CH_2 \xrightarrow{KOH} HC\equiv C-CH_2-CH_2-CH=CH_2.$$

Hydrogen halides are more easily removed from the halogen derivatives of dienes containing a -CH = CHCl [23,24] group, yielding enynes.

Isomerisation of multiple bonds sometimes occurs during the preparation of enynes from conjugated chlorodienes. Thus, the treatment of 2-chloropenta-1,3-diene with alkali yields vinylmethylacetylene[20,22], instead of the expected propenylacetylene:

$$CH_2=CCl-CH=CH-CH_3 \xrightarrow{KOH} CH_2=CH-C\equiv C-CH_3.$$

Migration of multiple bonds is also observed on dehalogenating allenic chlorides, e.g. 4-chlorobuta-1,2-diene[25], 1-chloro-3-methylbuta-1,2-diene[26], and 1-chloro-3-ethylpenta-1,2-diene[27], for instance:

$$CHCl=C=CR-CH_2-R \longrightarrow HC\equiv C-CR=CH-R.$$

The removal of hydrogen halides from the acetylenic halogen derivatives of the type $R-C\equiv C-CR_2^1Cl$ or $R'C\equiv C-CH_2-CHCl-R$ is only recommended for cases where R = aryl[28,29]. In other cases the yield of vinylacetylenes is usually small[30-34].

Metal acetylides can sometimes be used as acceptors for hydrogen halides[34-38]. For instance, the reaction of sodium acetylide with 1,3-dibromopropane besides hepta-1,6-diyne also yields, judging from the physical constants, vinylmethylacetylene[38]. However, the workers who studied this reaction wrongly assumed that they had obtained propenylacetylene.

The reaction of alcoholic alkali with 1,2,3,4-tetrabromoalkanes yields vinylacetylenes instead of the expected diacetylenes: a reduction takes place at the same time[39,40,41]. A convenient method for the preparation of vinylacetylene is the treatment of 1,2-dichlorobut-2-ene or the Δ^3-analogue with the solution of sodium amide in liquid ammonia[42]. Vinylacetylene can also be obtained in good yields by dehydrochlorinating 1,3-dichlorobut-2-ene (a by-product in the manufacture of chloroprene) with KOH in glycol[43]. Dehydrohalogenation also yields vinylacetylenic halogen derivatives[44,45] and ethers[46].

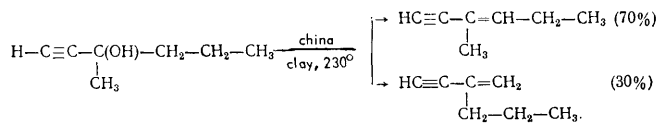
Vinylacetylene is formed in the reduction of some polyhalides by zinc[47,48].

2. Dehydration of Acetylenic Alcohols

This is a most convenient and frequently used general method for the preparation of enyne hydrocarbons, especially the branched ones. α-Acetylenic acid and alkylpropargyl alcohols are in their turn easily prepared from carbonyl compounds by Grignard reagents[49], Favorskii's reaction[14], or the reaction with acetylene and sodium amide in liquid ammonia[50]. β-Acetylenic alcohols can be prepared from propargyl bromide and aldehydes by Reformatski's reaction[51,52] or by the reaction of epoxides with acetylides in liquid ammonia[53].

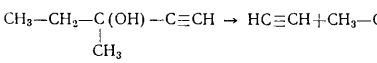
Dehydration of tertiary dialkylpropargyl alcohols is usually carried out by passing them over $MgSO_4$ [54,55] or $AlPO_4$ [56-58] at 230°–250°, or by heating them with 30% H_2SO_4 [59,60], acetic anhydride and H_2SO_4 [61], H_3PO_4 [62,63], or HCl [64]. There is a number of other dehydration catalysts: aluminium oxide[65-67], acid and basic sulphates[68-70], toluenesulphonic acid[71-73], china clay[74], $CuSO_4$ [75,76], oxalic acid[75,76], etc.[78-81]. The formation of enyne hydrocarbons has been repeatedly observed during the preparation of chlorides from dialkylpropargyl alcohols by the action of HCl [82-84]. In the dehydration of asymmetrically substituted dialkylpropargyl alcohols the hydrogen atom is split off mainly

from the larger radical, for instance [10,57,61,62,74,85,86]:

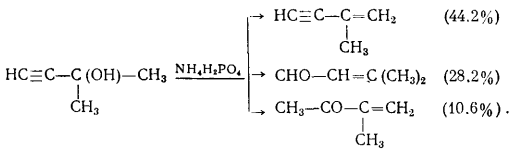


It was not possible to obtain 2-trifluoromethylbut-1-en-3-yne by the dehydration of the corresponding tertiary alcohol [87].

The dehydration of tertiary acetylenic alcohols with cyclic substituents can be carried out with $POCl_3$ in pyridine [88-92]. Tertiary acetylenic alcohols containing phenyl radicals are often dehydrated during distillation [93] or in the presence of acid reagents [94-95]. Dehydration in the presence of heterogeneous catalysts is often accompanied by the formation of considerable quantities of by-products [65,96,97]. Thus, over aluminium oxide, at 230°, alcohols are decomposed into acetylene and ketone to a considerable extent [65]:

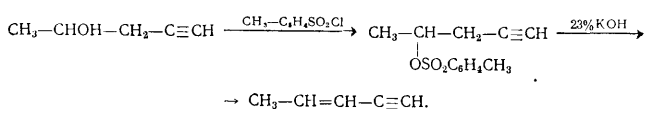


Over phosphates alcohols are isomerised to aldehydes and ketones [96,97]:

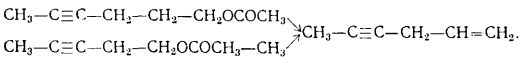


Acetylenic alcohols which do not contain the terminal ethynyl group yield better results [65,66]. Isomerisation of tertiary alcohols occurs under the action of formic acid or P_2O_5 in benzene [98]. Good yields of vinylacetylenic hydrocarbons are only obtained with aromatic alcohols [99].

Dehydration of secondary alkylpropargyl alcohols is more difficult: at 325° and over aluminium oxide hydrocarbons are only obtained from alcohols which do not contain the terminal ethynyl group [67]. For the preparation of hydrocarbons from β-acetylenic alcohols a method based on the preliminary formation of sulphonic esters can be used [100-104]:



Primary α- and secondary β-acetylenic alcohols can be converted to hydrocarbons by the pyrolysis of their respective acetates [105-107]:



Vinylacetylenic hydrocarbons can also be prepared by the pyrolysis of dialkylpropargyl phenyl ethers [108], and, possibly, of acetals containing a vinylethynyl group [109].

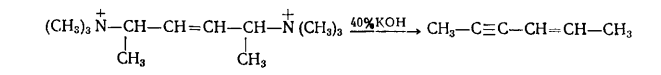
3. Splitting of the Elements of Alkylhypohalogenites from Acetylenic β-Halogeno-Ethers

Acetylenic β-halogeno-ethers are easily prepared by the action of metal acetylides on α, β-dibromo-ethers. The elements of alkylhypohalogenites are removed by heating with zinc, giving good yields of vinylacetylenic hydrocarbons [110,114]:

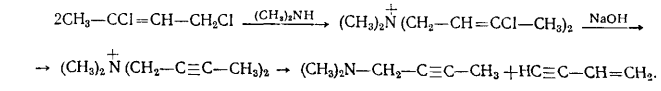
Vinylacetylene [110] and a series of its homologues and phenyl-substituted derivatives were prepared in this way, as well as some hydrocarbons containing isolated multiple bonds [114].

4. Exhaustive Methylation of Unsaturated Amines

Vinylacetylene [9,115,116] and vinylmethylacetylene [4-8,117,118] were first prepared by the decomposition of the products from the exhaustive methylation of unsaturated amines. The method was subsequently used repeatedly for the preparation of these hydrocarbons, and more recently for the preparation of hex-2-en-4-yne [119]:



A study was made of the synthesis of vinylacetylene by amination and subsequent exhaustive methylation of 1,3-dichloro but-2-ene, a by-product in the manufacture of chloroprene. Vinylacetylene was recovered in yields above 70% [115,116]:



5. Selective Hydrogenation of Diacetylenes

This reaction usually yields dienes [120]. In some cases, however, it is possible to stop the hydrogenation at the enyne stage. For instance, the reduction of hydrocarbons containing one of the triple bonds in the terminal position by sodium in liquid ammonia yields the corresponding enyne hydrocarbons as the terminal triple bond resists hydrogenation [121]. This method has no preparative importance as diacetylenes are not easily accessible.

B. PREPARATION FROM COMPOUNDS WITH A SMALLER NUMBER OF CARBON ATOMS

1. Dimerisation of Acetylenic Hydrocarbons

Soon after its discovery [1], the polymerisation of acetylene to mono- and divinylacetylenes in the presence of copper complexes was reproduced by Klebanskii [122-143] and Zelinskii [124]; Nieuwland et al. had not given a detailed account regarding the procedure. Many papers and patents [122-143] are devoted to the mechanism and the conditions of this reaction, which is the basis of the production of chloroprene from acetylene. The main difficulty lies in arresting the polymerisation at the dimer stage, i.e. monovinylacetylene, and various improvements of the original method concern this particular

step. If no special measures are taken, the reaction products are two trimers (divinylacetylene and ethynylbutadiene) and higher polymers.

In Klebanskii's opinion an ionic mechanism underlies acetylene polymerisation, the principal part being played by the acidic properties of acetylene complexes with cuprous chloride[122,125,126]. Different variations of the ionic mechanism were also suggested by other investigators[132,134]. Hypotheses involving the intermediate formation of copper acetylides or of copper acetylide complexes were also advanced[125,131].

This reaction cannot be used effectively for the synthesis of vinylacetylene homologues, although by this method acetylene and methylacetylene yielded small amounts of vinylmethylacetylene[144]:

$$CH_3{-}C{\equiv}CH + HC{\equiv}CH \longrightarrow CH_3{-}C{\equiv}C{-}CH{=}CH_2.$$

A series of workers showed vinylacetylene to be the primary product in acetylene polymerisation under different conditions[128], including the photochemical reaction[145,146] and the high-temperature and electrical cracking[143,147-151]. Vinylacetylene can be isolated from acetylene mixtures obtained by pyrolysis. A number of papers and patents[152-162] are devoted to the isolation of vinylacetylene from various gas mixtures, as well as to the analysis and purification of such mixtures.

2. Reactions of Metal Acetylides with Halogen Derivatives

These were used chiefly for the synthesis of enyne hydrocarbons with isolated multiple bonds. In the reaction of acetylenic Grignard reagents, or sodium acetylides with allyl bromide or allyl benzenesulphonate, good yields of allylacetylene and a series of its homologues were obtained[163-166]:

$$R{-}C{\equiv}C{-}MgBr + Br{-}CH_2{-}CH{=}CH_2 \xrightarrow{CuCl} R{-}C{\equiv}C{-}CH_2{-}CH{=}CH_2.$$

The reaction of allyl bromide with sodium acetylide gave a small yield of vinylmethylacetylene (I) involving a multiple bond migration[167]. The main reaction product was a hydrocarbon of structure (II):

$$HC{\equiv}CNa + Br{-}CH_2{-}CH{=}CH_2 \begin{cases} \rightarrow CH_3{-}C{\equiv}C{-}CH{=}CH_2 & (I) \\ \rightarrow HC{\equiv}C{-}\underset{\displaystyle CH{=}CH_2}{\underset{|}{CH}}{-}CH_2{-}CH{=}CH_2 & (II). \end{cases}$$

This method can be used for preparing aliphatic, alicyclic, and aromatic enyne hydrocarbons with one or several carbon atoms separating the multiple bonds[168-172]. There are patents on this subject, but they require testing[173].

Propargyl organometallic compounds can also react with active halogen derivatives, to yield enyne hydrocarbons[174].

3. Reactions of Propargyl Halides with Unsaturated Organometallic Compounds

These reactions, for instance with vinyl- and allyl-magnesium bromide also give enyne hydrocarbons, but in some cases they are obtained with an admixture of the isomeric vinylallenes[169,175,176]:

$$HC{\equiv}C{-}CH_2Br + BrMg{-}CH{=}CH_2 \begin{cases} \longrightarrow HC{\equiv}C{-}CH_2{-}CH{=}CH_2 \\ \longrightarrow CH_2{=}C{=}CH{-}CH{=}CH_2. \end{cases}$$

4. Alkylation of Vinylacetylene

Alkylation of vinylacetylene and its homologues containing a terminal ethynyl group is a convenient method for preparing vinylalkylacetylenes. The reaction is usually carried out in liquid ammonia with sodium amide. Alkyl halides and dialkyl sulphates are used as alkylating agents. This method was used for preparing vinylalkynes with alkyl radicals ranging from methyl to octyl inclusive, in yields of 80%. With the lower alkyl groups, the yield was diminished owing to the evaporation of the hydrocarbon together with the ammonia[177-179]. In some cases of alkylation in the presence of excess sodium amide the migration of multiple bonds towards the end of the molecule was observed[180]. This reaction does not work with secondary or tertiary alkyl halides.

$$R{-}Br + NaC{\equiv}C{-}CH{=}CH_2 \longrightarrow R{-}C{\equiv}C{-}CH{=}CH_2.$$

Good results are also obtained in alkylations of vinylacetylene Grignard reagents[181].

5. The Wittig Reaction

The Wittig reaction can be used for preparing enyne hydrocarbons from saturated halogen derivatives and acetylenic aldehydes according to the scheme[182].

$$R{-}CH_2Br \xrightarrow{(C_6H_5)_3P} [R{-}CH_2\overset{+}{P}(C_6H_5)_3]\,\overset{-}{Br} \xrightarrow{C_6H_5Li} R{-}CH{=}P(C_6H_5)_3 \rightarrow$$
$$\xrightarrow{HC{\equiv}C{-}CHO} R{-}CH{=}CH{-}C{\equiv}CH.$$

C. PREPARATION OF ENYNE HYDROCARBONS FROM COMPOUNDS WITH A LARGER NUMBER OF CARBON ATOMS. DECOMPOSITION OF ACETYLENIC GLYCOLS

Decomposition of vinylacetylenic tertiary alcohols with alkali[183,184] yields vinylacetylenes:

$$R_2C(OH){-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{KOH} R_2CO + HC{\equiv}C{-}CH{=}CH_2.$$

Vinylacetylenes are also obtained by the decomposition in the presence of sulphuric acid of some acetylenic glycols containing phenyl groups[185,186]:

$$C_6H_5{-}C{\equiv}C{-}\underset{\displaystyle CH_3}{\underset{|}{C}}(OH){-}\underset{\displaystyle CH_3}{\underset{|}{C}}(OH){-}C_6H_5 \rightarrow C_6H_5{-}C{\equiv}C{-}CH{=}CH_2 + CH_3{-}CO{-}C_6H_5.$$

II. PHYSICAL PROPERTIES OF ENYNE HYDROCARBONS

Only the first member in the series of vinylacetylenic hydrocarbons is gaseous at room temperature. The other hydrocarbons are liquid or solid. The physical properties

of vinylacetylene have been studied in greater detail than those of other enyne hydrocarbons. Its principal constants are given in Table 1.

TABLE 1. The principal physical constants of vinylacetylene.

Boiling point (760 mm) [187]	5.11°C	refractive index n_D (t°) [190]	1.4161
Vapour pressure [1,188]		thermal conductivity ($\lambda \times 10^4$ at 70°) [191]	0.437
at -10°C	401.0 mm	heat capacity (C_p°) [191,192]	
at 0°C	621.0 mm	at 298.16°K	17.49 cal × × deg^{-1} mole^{-1}
at +12°C	952.0 mm	at 1500°K	37.52 cal × × deg^{-1} mole^{-1}
Density [1,189]		viscosity ($\eta \times 10^4$)	
at -10°C	0.7187	at 40°C [191]	0.865
at 0°C	0.7095	solubility in water	
at +30°C	0.6679	at 0°C [193]	1.04%

Intermediate vapour pressures of vinylacetylene can be calculated from the formula

$$\log P_{(mm)} = 6.08797 - \frac{620.161}{187.960\ t^0}\ ^{194},$$

and those of the specific gravity in the temperature range from -3° to -80°, from the formula

$$d_4^t = 0.7095 - 0.00114\,t^0\ ^{142}.$$

The effect of an electric field [195] on the thermal conductivity of gaseous vinylacetylene was also studied. Heats of evaporation were not determined experimentally, but they were calculated for the temperature range -80° to +168° [195,197] and tabulated.

Data are available on certain other thermodynamic functions [192,198-202]. The energy of the first electron in excited state was calculated [203]. Explosive properties of vinylacetylene have been investigated [204,205]: concentrations in

TABLE 2. Principal constants of enyne hydrocarbons.

Hydrocarbon	B.p., °C	d_4^{20}	n_D^{20}	Method of prep.	Reference
$HC\equiv C-CH=CH-CH_3$	46—48	—	1.4356(19)	A2	33
cis	44.5—44,6	—	1.4377(16.5)	A2	100
trans	52—52.2	—	1.4407(16.5)	A2	100
	51.9	0.7270	1.4377	A2	101
$HC\equiv C-CH=CH-C_2H_5$	72—74	0.7425	1.4381	A2	51
$HC\equiv C-CH=C(CH_3)_2$	81—83	0.7537	1.4504	B4	180
	73—75	—	—	A2	70
$HC\equiv C-CH=CH-CH(CH_3)_2$	117—120	—	—	A1	11
$HC\equiv C-CH=CH-C_4H_9$	126—129	—	1.4431(22)	A2	103
$HC\equiv C-CH=CH-CH_2CH(CH_3)_2$	126—129	—	—	A1	12
$HC\equiv C-CH=CH-C(CH_3)_3$	?—	—	—	—	207
$HC\equiv C-CH=CH-C_4H_{13}$	57—58(11)	0.7822	1.4508	A2	104
$HC\equiv C-CH=CH-C_6H_{13}$	65(10)	—	1.4500(22)	A2	103
$HC\equiv C-CH=CH-C_{11}H_{23}$					
cis	m.p. 41—42°	—	—	B5	182
trans	m.p. 46.5—47.5°	—	—	B5	182
$HC\equiv C-C(CH_3)=CH_2$	32—32.5	0.7044	1.4151	A2	207
	32—32.5	—	1.4158	A2	10
$HC\equiv C-C(CH_3)=CH-CH_3$	67—69	—	1.4332	A2	10
	66—67	0.739	1.4310	A2	75
$HC\equiv C-C(CH_3)=CH-CH_2-CH_3$	91—94	—	1.4304(22)	A2	86
	93	—	—	A2	85
$HC\equiv C-C(CH_3)=CH-C_2H_7$	44—45(50)	0.776	1.4395	A2	74
$HC\equiv C-C(CH_3)=CH-CH(CH_3)_2$	104.5	—	—	A2	61
$HC\equiv C-C(CH_3)=CH-C_4H_{11}$	53(11)	—	1.4464(22)	A2	57
$HC\equiv C-C(CH_3)=CH-CH_3$	96.5	0.7886(25)	1.4338(25)	A2	72
C_2H_5	41—43(100)	0.7733(13)	1.4396(a,13)	A2	26
$HC\equiv C-C(C_3H_7)=CH-C_2H_5$	136—137	0.7799(25)	1.4432(25)	A2	72
$HC\equiv C-C(CH_3)=C(CH_3)_2$	41(30)	0.7916	1.4532	A2	74
$CH(CH_3)_2$					
$HC\equiv C-C(CH_3)=CH_2$	97.5—98	0.7544	1.4330	A2	207
$C(CH_3)_3$	98	0.7643(16.5)	1.4280(a,16.5)	A2	54
$HC\equiv C-C(CH_3)=CH-CH_3$	123—124	—	1.4470	A2	98
$C(CH_3)_3$					
$HC\equiv C-C(CH_3)=CH_2$	128	—	1.4410	A2	9
$C(CH_3)_2-C_2H_5$					
$HC\equiv C-C(CH_3)=CH-CH_3$	148	—	1.4500	A2	98
$C(CH_3)_2-C_2H_5$					
$CH_3-C\equiv C-CH=CH_2$	59—59.5	0.7402	1.4490	B4	208
	59.4	0.7339(25)	1.4467(25)	A4	6
$C_2H_5-C\equiv C-CH=CH_2$	83.5—84	0.7486	1.4519	B4	208
	83(747)	0.7480	1.4523	B4	181
$C_3H_7-C\equiv C-CH=CH_2$	108.5—109	0.7626	1.4626	B4	208
	44.3—44,7 (77)	0.7579(25)	1.4520(25)	A3	111
$C_4H_9-C\equiv C-CH=CH_2$	62—62.5(60)	0.7713	1.4560	B4	208
	61.5—62(60)	0.7671(25)	1.4505(25)	A3	111
$(CH_3)_2CH-CH_2-C\equiv C-CH=CH_2$	54—56(60)	0.7668	1.4440	B4	178
$C_6H_{11}-C\equiv C-CH=CH_2$	59.5—60(20)	0.7782	1.4580	B4	179
	27.7—28.2 (4)	0.7602(25)	1.4487(25)	A3	111
$(CH_3)_2CH-(CH_2)_2-C\equiv C-CH=CH_2$	76—77(60)	0.7803	1.4571	B4	178
$C_6H_{13}-C\equiv C-CH=CH_2$	76—76.5(20)	0.7873	1.4598	B4	179
	45—45.5(4)	0.7872(25)	1.4565(25)	A3	111
$C_7H_{15}-C\equiv C-CH=CH_2$	74.5(9)	0.7962	1.4606	B4	177
$C_8H_{17}-C\equiv C-CH=CH_2$	110.5—111 (20)	0.7964	1.4620	B4	179
	77.5—78(4)	0.7858(25)	1.4510(25)	A3	111
$CH_3-C\equiv C-CH=CH-CH_3$	88—89	0.7710	1.4918	A4	119
	91—92	0.7703	1.4634	A2	67
$C_4H_9-C\equiv C-CH=CH-CH_3$	70—70.5(29)	0.7832(25)	1.4590(25)	A3	111
$C_5H_{11}-C\equiv C-CH=CH-CH_3$	54.5—55(5)	0.7850(25)	1.4609(25)	A3	111
$C_6H_{13}-C\equiv C-CH=CH-CH_3$	45—45.4(4)	0.7872(25)	1.4565(25)	A3	111
$CH_3-C\equiv C-CH=C(CH_3)_2$	56—57(90)	0.7849	1.4659	A2	67
$CH_3-C\equiv C-C(CH_3)=CH_2$	82—83	0.7518	1.4512	B4	179
CH_3	75—77	—	1.4002	A2	108
$C_2H_5-C\equiv C-C(CH_3)=CH_2$	104.5—105.5	0.7572	1.4518	B4	179
CH_3					
$C_2H_7-CH(CH_3)-C\equiv C-CH=CH_2$ / $CH_3-CH=C(CH_3)-C\equiv C-CH_3$ / C_2H_7	139—140	0.7622	1.4450	A1	37
$(CH_3)_2C-C\equiv C-C(CH_3)=CH_2$?	58(100)	0.7622	1.4385	A1	35
$CH_3-C\equiv C-C(CH_3)=CH_2$	59—60(50)	0.7808	1.4518	B4	179
$C(CH_3)_3$					
$C_2H_5-C\equiv C-C(CH_3)=CH_2$	74—74.5 (50)	0.7774	1.4518	B4	179
$C(CH_3)_3$					
$CH_3-C\equiv C-C(CH_3)=CH-CH_3$	107—108	0.7883	1.4480	A2	84
CH_3					
$(CH_3)_2CH-C\equiv C-C(CH_3)=CH-CH_3$	67—70(30)	—	1.3949(22)	A2	66
CH_3					
$CH_3-C\equiv C-C(CH_3)=CH-C_4H_9$	80—85(30)	—	1.4158(22)	A2	66
CH_3					
$C_4H_9-C\equiv C-C(CH_3)=CH-CH_3$	80—82(30)	—	1.4638(22)	A2	65
CH_3					
$(CH_3)_2C-C\equiv C-C(CH_3)=CH-CH_3$	75—80(30)	—	1.3881(22)	A2	66
CH_3					
$C_4H_9-C\equiv C-C(CH_3)=CH-C_2H_5$	94—97(30)	—	1.4662(22)	A2	72
CH_3					
$C_4H_9-C\equiv C-C(CH_3)=CH-C_4H_9$	149—152(30)	—	1.4662(22)	A2	72
CH_3					
$C_4H_9-C\equiv C-C(CH_3)=C(CH_3)_2$	115—117(15)	—	1.4668(22)	A2	66
$CH(CH_3)_2$					
$(CH_3)_2C-C\equiv C-C(CH_3)=C(CH_3)_2$	58.5(7)	0.7778	1.4518	A1	36
$CH(CH_3)_2$					
$HC\equiv C-CH_2-CH=CH_2$	41.5—42.5	0.7246	1.4152(19)	A3	114
	42—43	0.7320(19)	1.4184(19)	B3	175

TABLE 2 (contd.)

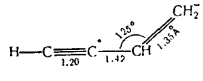
Hydrocarbon	B.p., °C	d_4^{20}	n_D^{20}	Method of prep.	Reference
$HC\equiv C-CH_2-CH=CH-CH_3$	75—76	0.7558	1.4290	A3	114
$HC\equiv C-CH_2-CH=CH-C_2H_5$	102	0.7635	1.4375	A3	114
$HC\equiv C-CH_2-CH=C(CH_3)_2$	101	0.771	1.4464	A2	63
$HC\equiv C-CH_2-C=C(CH_3)_2$ (CH₃)	112—113	0.788	1.4293	A2	63
$HC\equiv C-CH_2-C-C(CH_3)_2$ (CH₃)	126	0.799	1.4348	A2	63
$CH_3-C\equiv C-CH_2-CH=CH_2$	86—86.5	0.7630	1.4368	B2	166
	87(753)	0.767(14)	1.446(14)	A2	107
$C_4H_9-C\equiv C-CH_2-CH=CH_2$	58(22)	0.7770(25)	1.4413(25)	B2	165
$C_5H_{11}-C\equiv C-CH_2-CH=CH_2$	73—74(22)	0.7850(25)	1.4444(25)	B2	165
	73—74(22)	0.7880	1.4450	B2	163
$HC\equiv C-(CH_2)_2-CH=CH_2$	70	0.8579 (18.2)	—	A1	2
$HC\equiv C-(CH_2)_2-CH=CH-C_6H_7$ (*trans*)	144—145	—	1.4520—1.4525	B2	174
$C_5H_{11}-C\equiv C-(CH_2)_2-CH=CHC_5H_{11}$	?	—	—	—	209
$HC\equiv C-(CH_2)_3-CH=C(CH_3)_2$	128—129	0.7816(19)	1.4418(16)	B2	172
$HC\equiv C-(CH_2)_4-CH=CH_2$	122	—	1.4310—1.4325	B2	171
$HC\equiv C-(CH_2)_4-CH=CH-C_6H_7$	77—78(19)	—	1.4480(18)	A5	121
cis	73(10)	—	1.4462	B2	169
trans	82—84(18)	—	1.4462	B2	170
$HC\equiv C-C=CH-(CH_2)_3$	57—59(100)	0.8596	1.4891	A2	92
$HC\equiv C-C=CH-(CH_2)_4$	53—56(40)	—	1.4978	A2	88
	47—49(20)	0.9032	1.4956	A2	92
$HC\equiv C-C=CH-(CH_2)_5$	78(35)	—	1.4980(19)	A2	58
$HC\equiv C-C=CH-CH_2-CH(CH_3)-(CH_2)_2$	160	0.8560	1.4648	A1	21
$HC\equiv C-C=C(CH_3)-(CH_2)_3-C(CH_3)_2$	68—69(18)	—	1.4925(14)	A2	90
$CH_3-C\equiv C-C=CH-(CH_2)_4$	165—167	0.8600	1.4469	B4	21
$CH_3-C\equiv C-C=CH-CH_2-CH(CH_3)-(CH_2)_2$	175	0.859	1.4654	B4	21
$C_4H_9-C\equiv C-C=CH-(CH_2)_4$	68(0.6)	—	1.5000	A2	88
$C_4H_9-C\equiv C-C=C(CH_3)-(CH_2)_2-C(CH_3)_2$	133—134(12	—	1.4800	A2	90
$HC\equiv C-CH-CH=CH-(CH_2)_3$	97.2(752)	0.8014	1.4363	B2	168
$HC\equiv C-CH_2-C=CH-(CH_2)_4$	56(12)	—	1.4835(21,5)	—	70
$C_4H_{11}-C\equiv C-CH-CH=CH-(CH_2)_2$	120(15)	0.976	1.4809	B2	21
$C_4H_{11}-CH_2-C\equiv C-CH-CH=CH-(CH_2)_2$	150(15)	0.962	1.5048	B2	21
$C\equiv C-(CH_2)_3-CH=CH-(CH_2)_3$	100(20)	—	1.5078(25)	—	210
$HC\equiv C-CH-CH-C_6H_5$	59(2)	0.9640	1.6123	A1	29,52
	65—67(4)	0.9784	1.6047	A1	92
$C_6H_5-C\equiv C-CH=CH_2$	85—86(15)	0.9480	1.6018	A3	113
	96(20)	0.9480	1.6018	A1	28
$C_6H_5-C\equiv C-CH=CH-CH_3$	66—67(1)	0.9448	1.5893	A2	99
$C_6H_5-C\equiv C-CH=CH-C_6H_5$	71—72(1)	0.932	1.5802	A2	99
$C_6H_5-C\equiv C-CH=CH-C_6H_{11}$	110—111(1)	0.9167	1.5508	A2	77
$C_6H_5-C\equiv C-CH=CH-C_6H_5$	144—146(2)	—	1.5613	A2	19
$C_6H_5-CH_2-C\equiv C-CH=CH-CH_3$	40(04)	0.9450(26.5)	1.5510(26.5)	A2	19
$C_6H_5-C\equiv C-C=CH_2$ (CH₃)	87—89(7)	0.9425	1.5750 (α)	A2	94
$C_6H_5-C\equiv C-C=CH_2$ $C(CH_3)_2$	115—116(10)	—	—	A2	14
$C_6H_5-C\equiv C-C=CH-CH_3$ (CH₃)	113—115(9)	0.9305	1.5828(13)	A2	15,16
$C_6H_5-C\equiv C-C=C(CH_3)_2$ (CH₃)	120—122(12)	0.9254	—	A2	14
$C_6H_5-C\equiv C-C=CH-C_4H_{11}$ (CH₃)	141—142(5)	—	—	A2	178
$C_6H_5-C\equiv C-CH_2-CH=CH_2$	103—105(20)	0.940(15)	1.5580(18)	B2	164
	107—108(22)	0.932	1.5574	B2	165
$HC\equiv C-CH-CH_2-CH=CH_2$ C_6H_5	60.5—61 (1.6)	0.9214(25)	1.5228(25)	B3	176
$C_6H_5-C\equiv C-C=CH-(CH_2)_4$	167—170 (16)	—	—	A2	180
$C_6H_5-C\equiv C-CH=CH-(CH_2)_3$	160(15)	0.997	1.5516	B2	21
$(C_6H_5)_2C-C\equiv C-CH=CH_2$	134—135 m.p.			B4	450

Note: 1) The pressure at the boiling points is given in brackets. 2) The temperature at which the refractive indices and specific gravities were measured is given in brackets. Temperature is not indicated for the data obtained at 20°. 3) Hydrocarbons prepared by dehydration of unsymmetrical dialkylpropargyl alcohols (A2) consists of a mixture of two isomers. The formula given in the table is that of the predominant isomer. 4) The best available data on phenyl-substituted enynes have been selected.

explosive mixtures with air range from 2.13–22.92% [204]. The solubility of vinylacetylene in water decreases with rise in temperature and on saturation of the solution with sodium chloride [193].

The principal constants of vinylacetylene homologues and of other enyne hydrocarbons are given in Table 2 which shows that the boiling points of enyne hydrocarbons are closely dependent on their structure. For instance, of all the isomers with five carbon atoms, vinylmethylacetylene has the highest, and isopropenylacetylene the lowest boiling point. Hydrocarbons with conjugated multiple bonds have a higher boiling point than their isomers with the same skeletal structure but with isolated bonds. Vinylalkynes have the highest refractive index of all the hydrocarbons with conjugated multiple bonds and a straight chain. Attempts have been made to calculate densities and refractive indices of vinylacetylenes, as well as those of other hydrocarbons [211].

Electron-diffraction data. Electron-diffraction patterns for vinylacetylene and vinylmethylacetylene show their spatial configuration to be as follows [7,212]:



Few thermodynamic data are available for vinylacetylene homologues. They include heats of formation, heats of dissociation, and enthalpies for gaseous allyl-, isopropenyl-, and vinylmethylacetylenes [213], as well as the thermal conductivity of gaseous isopropenylacetylene [214] and its rate of combustion [215].

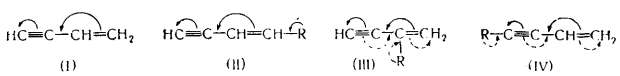
Molecular refractions found experimentally for enyne hydrocarbons with isolated multiple bonds are close to the calculated values. In the case of vinylacetylene, however, there is a considerable exaltation [216]. The highest exaltation is observed in the vinylalkyne series (1.1–1.4). The value falls when groups are attached to the β-carbon atom of the double bond. The exaltation of the molecular refraction of vinylacetylenes is somewhat lower than that of 1, 3-dienes.

TABLE 3. Dipole moments of vinylacetylene and its homologues.

Hydrocarbon	μ, Debye	Hydrocarbon	μ, Debye
$HC\equiv C-CH=CH_2$	0.77	$C_3H_7-C\equiv C-CH=CH_2$	0.65
$HC\equiv C-CH=CH-CH_3$, *cis*	0.85	$C_4H_9-C\equiv C-CH=CH_2$	0.63
trans	0.93	$C_5H_{11}-C\equiv C-CH=CH_2$	0.65
$HC\equiv C-C(CH_3)=CH_2$	0.55	$C_6H_{13}-C\equiv C-CH=CH_2$	0.67
$HC\equiv C-C(C(CH_3)_3)=CH_2$	0.69	$C_8H_{17}-C\equiv C-CH=CH_2$	0.68
$HC\equiv C-CH=CH-C_6H_5$	0.97	$C_6H_5-C\equiv C-CH=CH_2$	0.27
$CH_3-C\equiv C-CH=CH_2$	0.57	$CH_3-C\equiv C-C(CH_3)=CH_2$	0.65
$C_2H_5-C\equiv C-CH=CH_2$	0.62	$CH_3-C\equiv C-C(C(CH_3)_3)=CH_2$	0.67
		$C_2H_5-C\equiv C-C(C(CH_3)_3)=CH_2$	0.64

Dipole moments (Table 3) were measured for a series of enyne hydrocarbons of different structures containing conjugated multiple bonds[179,208,217]. Owing to conjugation, the dipole moment of vinylacetylene is somewhat lower than that of ethylacetylene (0.80 Debye). Substitution of the acetylenic hydrogen or the hydrogen attached to the β-carbon atom of the ethylenic bond by an alkyl or, especially, a phenyl radical results in a sharp drop in the dipole moment. On the other hand, the substitution of a terminal hydrogen of the vinyl group causes a sharp increase in the dipole moment. Dialkyl derivatives, with the substituents at the acetylenic and "inner" carbon atoms of the double bonds have dipole moments approximately the same as vinylalkynes.

Dipole-moment values support the hypothesis of the shift of electron density in vinylacetylenic hydrocarbons under the influence of substituents. The electron-density shift is represented by arrows in formulae (I)–(IV):



(I) (II) (III) (IV)

Ultra-violet spectra. Enyne hydrocarbons with isolated multiple bonds absorb only in the vacuum region [< 300 mμ (Ed. of Translation)]. Vinylacetylene, its homologues and derivatives give absorption maxima in the region at the limit of the sensitivity of ordinary spectrophotometers (~ 220 mμ) with a characteristic inflection at ~ 228 mμ. Diene hydrocarbons absorb in approximately the same region, but with higher intensity and without the inflection[81,100,218-224]. Aromatic vinylacetylenes give absorption maxima at ~ 250 mμ[81].

Infra-red spectra. Infra-red spectra of numerous vinylacetylenic hydrocarbons of different structure are available in the literature[100,121,179,192,223,225-232], but the theoretical frequencies have only been worked out for vinylacetylene[192,226,233].

Spectra of enyne hydrocarbons with isolated bonds consist of the ordinary absorption bands, characteristic of olefines and acetylenes of analogous structure[230]. In the spectra of vinylacetylene and its homologues the frequencies of the stretching vibrations of the triple, and especially the double bond, are considerably lower than in unconjugated systems. The stretching frequency of the double bond in the spectra of alkenylacetylenes is somewhat higher (1620 cm^{-1}) than in those of vinylalkynes (1608 cm^{-1})[230].

Frequencies characteristic of a terminal ethynyl group are 2114 and 3300 cm^{-1}, whereas disubstituted acetylenes absorb at 2230–2235 cm^{-1}. The intensity of the double-bond band is considerably higher for vinylalkynes and isoalkenylacetylenes, containing an unsubstituted methylene group, than for alkneylacetylenes. This property of the spectra may be related to the reactivity of the double bond with respect to electrophilic reagents[230].

The spectra of enynes exhibit a general pattern related to the structure of the hydrocarbons. For instance, characteristic high intensity bending frequencies near 910 and 972 cm^{-1} correspond to the vinyl group, a frequency near 955 cm^{-1}, to the $-CH=CH-$ group (of especially high intensity for the *trans*-isomer)[100], and a frequency at 890–900 cm^{-1}, to the isopropenyl group. Vinylalkynes have a high-intensity frequency for the stretching CH-vibrations at ~3100 cm^{-1}. Most vinylacetylenes absorb at 1660–1790 cm^{-1}, a frequency characteristic of acetylenes, but of unexplained origin. The presence of a t-butyl radical gives rise to absorption in the region 1200–1250 cm^{-1}[179,230].

In the spectra of phenyl-substituted vinylacetylenes the enyne system is characterised by frequencies of 1600, 2094, and 2103 cm^{-1} for monosubstituted, and 1631, 2184, 2200–2220, and 2245 cm^{-1} for disubstituted acetylenes. Thus, the vibration frequencies corresponding to the double bond are lower than those for olefines when the bond is located between the phenyl and acetylenic groups[18,231].

Infra-red spectra can be used for the determination of vinylacetylene impurities in industrial products[232].

Raman spectra have been studied to a lesser degree than infra-red[35,36,52,233-237]. In the Raman spectra of vinylalkynes the double bond is represented by the high-intensity frequency of ~ 1606 cm^{-1} and in those of alkenylacetylenes by the frequency of ~ 1616 cm^{-1}. The terminal ethynyl group is characterised by a high-intensity frequency of ~ 2100 cm^{-1}, and a low intensity one of ~ 3300 cm^{-1}, and the disubstituted acetylenic group, by frequencies of 2230 (very high intensity) and 2330 cm^{-1} (medium intensity)[215]. In the spectra of allylacetylene and allylmethylacetylene the triple bond gives rise to a high-frequency band of 2124 cm^{-1} (there is no conjugation)[216,236]. Bending CH vibrations of ethylenic groups are represented by a medium-intensity frequency of 920 cm^{-1}, or a low-intensity one of 950 cm^{-1} (depending on the structure).

The conjugated system in aromatic vinylacetylenes is characterised by frequencies as follows:
$C_6H_5-CH=CH-C\equiv CH$ 1611, 2104 cm^{-1}; and
$C_6H_5-C\equiv C-CH=CH_2$ 1630, 2186, and 2223 cm^{-1}[18,237].

Microwave spectra have been studied only for vinylacetylene[238].

Mass-spectra have been measured for vinylacetylene and 6 homologues of different structure[239-242]. The highest intensity in the mass-spectra of vinylacetylene and its three nearest homologues are due to molecular ions. Ionised residues are formed primarily by the rupture of the

C–H bond. The curve, obtained for the homologues by plotting the ion distribution against the number of carbon atoms contains two maxima (for $C_3H_x^+$ and $C_5H_x^+$ ions). The first one is characteristic of all hydrocarbons. Of all ions formed by the breaking of the C–C– bond, the one with a mass of 39 has the highest energy. Further loss of hydrogen by the initially formed ionised residues is characteristic of all isomers.

Determinations of ionisation potentials showed isopropenylacetylene to be the most difficult to ionise (ionisation potential 10.1 eV). Vinylmethylacetylene (9.4 eV) and especially propenylacetylene (8.5 eV) have considerably lower ionisation potentials than vinylacetylene (9.9 eV).

Increase in the chain length of the radical attached to the triple bond results in reduced stability of the molecular ion and an increase in the energy of ionised residues formed by the breaking of C–C– bonds. $C_3H_x^+$ and $C_6H_x^+$ ions have the maximum energy. The ions predominating among the ionised residues — $C_nH_{2n-3}^+$, $C_nH_{2n-5}^+$, $C_nH_{2n-7}^+$, as well as $C_nH_{2n-4}^+$ — are probably stabilised by conjugation. The ionisation potential drops with increase in chain length.

Polarographic curves have been obtained for 12 vinylacetylenic hydrocarbons of different structure[243,244]. Only conjugated enynes are reduced at the dropping mercury electrode. Allylmethylacetylene, containing isolated multiple bonds, is not reduced[244].

Vinylacetylene ($E_{\frac{1}{2}}$ = 2.4 eV) is reduced rather more easily than butadiene, and with greater difficulty than diacetylene. The nearest homologues are more difficult to reduce than the unsubstituted compound ($E_{\frac{1}{2}}$ = 2.5–2.6 eV). The position of one methyl group in the chain has little influence on reduction potentials. Isopropenylacetylene is the compound most easily reduced. Increased length of the chain of the radical attached to the triple bonds results in some lowering of the half-wave potential. Substitution of an ethyl group by vinyl has no appreciable effect. Increase in length and branching of a radical attached to the double bond leads to a somewhat increased half-wave potential. Introduction of a second methyl group at the double bond has little effect on the potential. If, however, one methyl group substitutes the acetylenic hydrogen and another an ethylenic hydrogen, the potential is sharply increased (up to 2.8 eV).

The above peculiarities in the polarography of vinylacetylenic hydrocarbons can be most easily explained by the effect of the radicals on the adsorption of hydrocarbons by the mercury surface, without which the reduction is impossible.

III. CHEMICAL PROPERTIES OF ENYNE HYDROCARBONS

The chemical reactions of enyne hydrocarbons usually fall into two groups, determined either by multiple bonds, particularly by the conjugated vinylacetylenic system, or by the terminal acetylenic hydrogen atom. The first group includes additions, complex formations, homo- and heterocyclisations, and polymerisations. The second group covers substitutions of hydrogen by halogens, metals, and other elements, as well as condensations with carbonyl compounds.

A. REACTIONS OF MULTIPLE BONDS

1. Action of Oxidising Agents

Gaseous vinylacetylene is not oxidised by atmospheric oxygen. In the liquid phase it easily forms peroxides which remain, after the evaporation of vinylacetylene, as a yellow, explosive residue. In the presence of 5% chloroprene the oxidation rate of vinylacetylene is increased 5–6 times; in the presence of water it is halved. In the presence of 0.5–1% Neozone D (phenyl-β-naphthylamine) or the antioxidant from wood resin the oxidation by atmospheric oxygen does not take place[245]. Vinylacetylene and its homologues containing a terminal ethynyl group are oxidised by atmospheric oxygen in the presence of CuCl + NH_4Cl according to the following scheme[246,247]:

$$2R{-}CH{=}CH{-}C{\equiv}CH \xrightarrow{O_2} R{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}CH{=}CH{-}R.$$

Ozone primarily attacks the double bond. Typical of this reaction is the ozonolysis of deca-2,8-diene-4,6-diyne to diacetylenedicarboxylic acid[247]:

$$CH_3{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}CH{=}CH{-}CH_3 \xrightarrow{O_3} HOCO{-}C{\equiv}C{-}C{\equiv}C{-}COOH$$

With vinylbutyl- and isopropenylacetylenes the ozonolysis rate changes after the addition of 1 mole of ozone[248].

Hydrogen peroxide in formic acid reacts with vinylacetylene at the double bond[249,250]:

$$HC{\equiv}C{-}CH{=}CH_2 \longrightarrow HC{\equiv}C{-}CHOH{-}CH_2OH.$$

The reaction with peracids also takes place primarily at the double bond. For instance, the oxidation of hex-1-en-3-yne by benzoyl hydroperoxide yields the oxide previously prepared from the bromohydrin[251]:

$$C_2H_5{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{C_6H_5CO{-}OOH} C_2H_5{-}C{\equiv}C{-}CH(O)CH_2$$

$$C_2H_5{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{HOBr} C_2H_5{-}C{\equiv}C{-}CHOH{-}CH_2Br \xrightarrow{KOH} C_2H_5{-}C{\equiv}C{-}CH(O)CH_2$$

Acetyl, benzoyl, and phthalyl hydroperoxides react in the same manner with the phenyl derivatives of vinylacetylenes and dienynes[77,78,99,247,252,253].

In order to determine their structure, enyne hydrocarbons have often been oxidised by potassium permanganate to acids[54]. Vinylacetylene has been used as fuel, for instance in welding[198]. There are several patents available on the subject[254,255].

2. Hydrogenation

Hydrogenation of vinylacetylene has for a long time attracted attention as a key factor in the possible preparation of butadiene from acetylene. The first results were published as far back as 1935, by Lebedev[256] and Klebanskii and collaborators[257,258]. Their results, as well as those of the Japanese chemists[259,261], showed that hydrogenation of vinylacetylene over different palladium, platinum, and nickel catalysts yields a mixture of butadiene and the products of further hydrogenation. The yield of butadiene did not exceed 75–78% of the reacted acetylene. Neither ethylacetylene nor methylallene were observed in the mixture. The only strictly selective processes discovered were the electrochemical hydrogenation in weakly alkaline media at platinum electrodes, and reduction by means of $CrCl_2$.

Klebanskii et al.[262] attempted recently to improve the selectivity of the process, and develop an industrial method for the preparation of butadiene from vinylacetylene. On the basis of the data available in the literature and from their own results, they chose as catalyst palladium on silica gel. According to them the initial stage of the reaction is zero order with respect to vinylacetylene, and first order with respect to hydrogen. The apparent activation energy was ~ 10 000 cal/mole. Hydrogenation was practically selective up to 30%, the yield of butadiene being 90–95% with respect to reacted vinylacetylene. Later the hydrogenation of butadiene formed in the reaction began. Changes in catalyst carriers and solvents affected the hydrogenation rate, but not the selectivity. The latter is increased somewhat by the increase in temperature and rate of agitation, and is higher in neutral and acid than in alkaline media. The addition of catalyst poisons (H_2S, mercury and copper salts) lowers the selectivity. On the other hand, the addition of lead or copper acetates increases it[263].

Catalytic hydrogenation of vinylacetylene has been covered by many patents. Of special interest are those in which vinylacetylene is hydrogenated to butene and butanes in 87% yield. The mixtures obtained can be used to prepare 2,2,4-trimethylpentane (isooctane)[264,265]. There are patents on several reductions by nascent hydrogen, e.g. by means of zinc powder and alkali[266–268], potassium amalgam[269], etc. In the hydrogenation by the latter method some methylallene is formed. The formation of methylallene is also observed in catalytic hydrogenations under pressure over catalysts containing iron[270].

In the presence of catalysts vinylacetylene homologues can also add hydrogen selectively to their triple bond, but the process is to a greater or less extent followed by further hydrogenation of the dienes to olefines[92,271–273]. Alkenyl- and isoalkenylacetylenes, as well as their aromatic analogues, give dienes in good yields by hydrogenation over colloidal palladium. Under the same conditions the hydrogenation of vinylalkyl- and vinylarylacetylenes cannot be used as a preparative method for obtaining dienes, the latter being to a considerable extent simultaneously hydrogenated to olefines *. Hydrogenation of enyne hydrocarbons to dienes can be carried out over an iron catalyst under pressure[72,274]. Data are available on the exhaustive hydrogenation of enyne hydrocarbons to paraffins[28,52].

3. Addition of Halogens

The reaction of enyne hydrocarbons with fluorine has not been studied. Thermal and photochemical chlorination of vinylacetylene have been studied in the gaseous phase at 60°—150° and 650 mm Hg. At ordinary temperatures polymerisation occurs extensively, whereas at higher temperatures mainly tetrachlorides are formed. In chlorinations under pressure explosions with the separation of carbon were observed. Chlorination at 120° gave a dichloride of b.pt. 35° (40 mm Hg), namely 1,2-dichloro-buta-1,3-diene[275]

The chlorination of vinylacetylene in very dilute chloroform solution, at low temperatures (down to -60°) and with a deficiency of chlorine, can yield small quantities of dichlorides. All possible isomers are formed with allenic (III) and acetylenic (I) dichlorides predominating[45,276]:

$$H-C\equiv C-CH=CH_2 \xrightarrow{Cl_2} \begin{cases} \rightarrow HC\equiv C-CHCl-CH_2Cl & (I) \\ \rightarrow CHCl=CCl-CH=CH_2 & (II) \\ \rightarrow CHCl=C=CH-CH_2Cl & (III). \end{cases}$$

During the chlorination of vinylethylacetylene large quantities of high-boiling products are formed. Nevertheless, the acetylenic dichloride, containing small quantities of 1,3-diene dichloride, predominates in the mixture. 1,4--Addition does not take place.

Bromination of vinylacetylene in chloroform solution[277] gives good yields of dibromides. As in chlorination, all possible isomers are formed, with allenes and dienes predominating. The relative yield of allenic dibromide is increased by lowering the temperature[278]. It seems that the dienic dibromide is formed partly by isomerisation of the allenic product. The nature of bromine addition to vinylacetylene homologues depends on the structure of the compounds involved. Non-conjugated enyne hydrocarbons and vinylalkynes add bromine exclusively to their double bond[43,166,279,280]:

$$CH_3-C\equiv C-CH_2-CH=CH_2 \xrightarrow{Br_2} CH_3-C\equiv C-CH_2-CHBr-CH_2Br,$$

$$CH_3-C\equiv C-CH=CH_2 \xrightarrow{Br_2} CH_3-C\equiv C-CHBr-CH_2Br.$$

Isopropenylacetylene also adds bromine[281]. Alkenylacetylenes yield primarily allenic dibromides with small quantities of 1,3-dienic dibromides. Acetylenic dibromides are not formed at all[281,282].

$$CH_3-CH=CH-C\equiv CH \xrightarrow{Br_2} CH_3-CHBr-CH=C=CHBr.$$

In all cases allenic and acetylenic dibromides are easily isomerised to 1,3-diene dibromides under the influence of CuBr and HBr. The preparation of tetrabromides from enyne hydrocarbons has been achieved repeatedly[2,28,29,52,43,166,275,277].

The addition of iodine to enyne hydrocarbons with isolated multiple bonds leads to both possible diiodides, together with the tetraiodides[283]. Vinylacetylenic hydrocarbons add iodine primarily to their triple bond, regardless of structure. The reaction only proceeds in light[283,284]. Their reaction with interhalogen compounds has also been studied. Iodine monochloride adds in the same way as bromine, but the action of iodine monobromide resembles more that of iodine[45].

Analogous behaviour is observed in the additions of halogens to vinylacetylenic alcohols and esters[285,286].

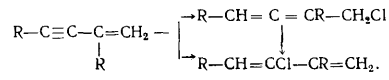
4. Addition of Hydrogen Halides

The reaction of vinylacetylenic hydrocarbons with hydrogen halides has been studied thoroughly, as it is involved in the production of such valuable synthetic rubber monomers as chloroprene and fluoroprene[287]. Hydrogen fluoride unites with vinylacetylene and isopropenylacetylene at the 1,2-position in the presence of mercury compounds, yielding fluoroprene. Another molecule of hydrogen fluoride adds at the same position[288–291]:

$$HC\equiv C-CH=CH_2 \xrightarrow{HF} CH_2=CF-CH=CH_2 \xrightarrow{HF} CH_3-CF_2-CH=CH_2.$$

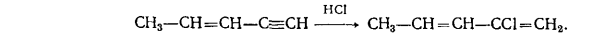
* It should be noted that in the hydrogenation of ethynylcyclohexene over Pd/Ni, vinylcyclohexene was obtained only in 12% yield[476], but in the hydrogenation over colloidal palladium or Pd/$CaCO_3$ the yields were good[92,220].

Without a catalyst, hydrogen chloride and bromide react with vinylacetylene, and alkenyl-, and isoalkenylacetylenes at 1,4- and 1,2- positions [71,292,293]. In the presence of catalysts only 1,2- addition products are obtained [71,73,178,294-301]:



In the case of ethylvinyl- and isopropenylacetylenes hydrogen bromide reacts also with the ethylenic bonds, but yields of these products are small [302]. The second molecule of hydrogen halide is added at 1,4-position, yielding, in the case of vinylacetylene, 1,3-dihalogeno-but-2-enes.

In contrast to the above hydrocarbons, alkenylacetylenes add hydrogen chloride and bromide at 1,2- or 1,4-positions in the absence of catalysts [302,303]:



Enyne hydrocarbons with isolated multiple bonds add hydrogen halides to the triple bond [166,279].

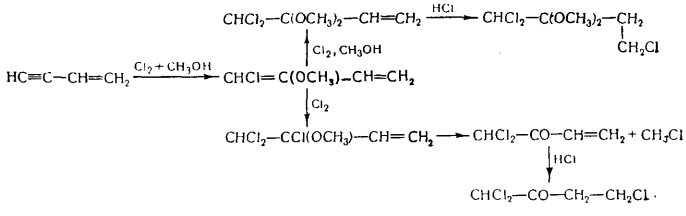
Thus, in all cases, regardless of the structure of the enyne hydrocarbon, the addition of the proton attacking the molecule occurs exclusively, or almost exclusively, at the acetylenic bond. The position of attachment of the anion depends on the structure of the hydrocarbon and reaction conditions. It seems that hydrohalogenation proceeds via a π-complex.

Hydrochlorination and hydrofluorination of vinylacetylene are described in a large number of papers and patents [287]. A method has been devised for separating diacetylene from vinylacetylene by removing the latter in the form of chloroprene after reaction with HCl [304].

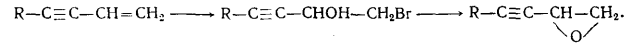
5. Addition of Hypohalogenous Acids and Esters

The reaction of vinylacetylene with halogeno-amides in aqueous and alcoholic solutions yields a complex mixture of products. As with the addition of hypohalogenites, substitution of the acetylenic hydrogen by halogen occurs, the compound obtained subsequently reacts further with hypohalogenites [305].

The action of chlorine on methanolic vinylacetylene gave a small yield of impure 1-chloro-2-methoxybuta-1,3--diene and a series of products of its subsequent transformations [306]:

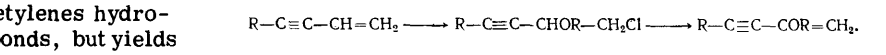


Addition of hypobromous acid to vinylalkylacetylenes by means of bromoacetamide in aqueous solution gave only the product of addition of HOBr at the double bond [307]:



Acetylonic epoxides were prepared from such addition products.

The reaction of benzenedichloro- and benzenedibromosulphonamides with ethanolic solutions of vinylalkylacetylenes also leads to the addition of alkylhypohalogenites at the double bond only. The acetylenic β-bromo-ethers thus obtained give alkoxyvinylacetylenes on dehydrohalogenation [305,308]:

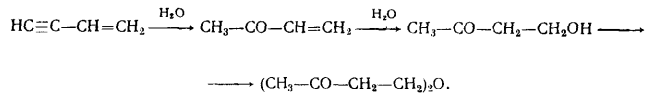


Thus, it was established that, like bromine, hypobromous acid and its esters are added at the double bond of vinylalkynes. This type of addition was explained by the shift of electron density in the hydrocarbons towards the double bond under the influence of substituents.

Dialkenylacetylenic hydrocarbons add hypobromites at at the double bond. Thus in the case of vinylisopropenylacetylene the addition takes place at the isopropenyl group Vinylalkynols behave similarly with respect to hypoiodites [309]. Enyne hydrocarbons with non-conjugated bonds also add hypobromites primarily to the ethylenic bond, but with a smaller selectivity [166].

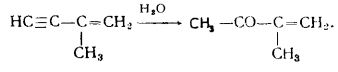
6. Addition of Water, Alcohols, Acids, and Phenols

The reaction of vinylacetylene with water in the presence of Kucherov's catalyst gives good yields of methyl vinyl ketone. A number of papers and patents are devoted to the development of this method. The by-products in the reaction are 3-oxobutanol and 3-oxobutyl ether [310]:



Some patents claim the formation of diacetyl in this reaction [311,312]. In the presence of the same catalyst, and in solution of different alchols, vinylacetylene yields methyl β-alkoxyethyl ketones; in phenol solution, methyl β-phenoxyethyl ketone is formed and, in solutions of organic acids, methyl β-acyloxyethyl ketones [313-315].

Methyl vinyl ketone can be prepared by the hydration of vinylacetylene in the gaseous phase at 325°–400° over cadmium tungstate, zinc oxide, or cadmium calcium phosphate catalysts. The first catalyst is the most active: at 325° and in the presence of ten times the theoretical amount of steam it gives methyl vinyl ketone in 87% yield. The by-products in this reaction are the dimer of methyl vinyl ketone (2-acetyl-6-methyl-2,3-dihydropyran) and vinylacetylene polymers [316]. Vinylacetylene homologues containing a terminal vinylethynyl group can also be hydrated to corresponding ketones. Aldehydes were not observed in any of the reactions [56,121,317-320].



The same type of water addition also takes place in hydrations by means of $HgSO_4$ in alcoholic solutions [314], in the presence of mercuric acetate in acetic acid [319] and by means of 80% formic acid [320]. The addition of water to this type of enyne therefore strictly obeys Markownikoff's rule.

Hydration of vinylalkynes under the conditions of Kucherov's reaction[321,322], as well as in the gaseous phase over cadmium calcium phosphate catalyst[323] takes a different couse: oxygen is added primarily not to the middle, but to a terminal atom of the conjugated system, and the alkyl allyl ketones (I) formed are isomerised in acid media to alkyl propenyl ketones (II).

$$R-C\equiv C-CH=CH_2 \xrightarrow{H_2O} \underset{(I)}{R-CO-CH_2-CH=CH_2} \xrightarrow{[H^+]} \underset{(II)}{R-CO-CH=CH-CH_3}.$$

Such hydration could be explained by 1,4-addition of water. However, it also takes place in the case of non-conjugated enynes, e.g. methylallylacetylene, where 1,4-addition is not possible[324,325].

$$CH_3-C\equiv C-CH_2-CH=CH_2 \xrightarrow{H_2O} \begin{cases} CH_3-CO-CH_2-CH_2-CH=CH_2\ (85\%) \\ CH_3-CH_2-CO-CH_2-CH=CH_2 \\ \downarrow \\ CH_3-CH_2-CO-CH=CH-CH_3\ (15\%). \end{cases}$$

Water is added to the acetates of the corresponding alcohols[326] in the same way as to the vinylalkynes. The ethers from such alcohols, however, form methoxyalkyl vinyl ketones after the addition of water[327]. Chlorides, alcohols, ethers, esters, and amines of the type $R-C\equiv C-CH_2X$ form, by hydration, only ketones of the type $R-CO-CH_2-CH_2X$[326-330]. This behaviour is complicated by the fact that, quite unexpectedly, isopropenylalkynes are hydrated, in 90% yield, in the opposite sense, i.e. they behave like isopropenylacetylene itself:

$$\underset{\substack{|\\CH_3\\(V)}}{CH_3-C\equiv C-C=CH_2} \xrightarrow{H_2O} \underset{|\\CH_3}{CH_3-CH_2-CO-C=CH_2}.$$

Similarly, the hydration of vinylisopropenylacetylene yields only propenyl isopropenyl ketone[332]:

$$\underset{|\\CH_3}{CH_2=C-C\equiv C-CH=CH_2} \xrightarrow{H_2O} \underset{|\\CH_3}{CH_2=C-CO-CH_2-CH=CH_2} \xrightarrow{[H^+]}$$

$$\longrightarrow \underset{|\\CH_3}{CH_2=C-CO-CH=CH-CH_3}.$$

Oxygen is, therefore, always linked to the most substituted carbon atom.

Hydration rules for vinylacetylenic hydrocarbons do not seem to be connected with electron shifts within the molecules under the influence of substituents (see formula on p. 495). Such shifts occur in opposite directions in hydrocarbons of types (II) and (III), and yet they add water in the same way. In hydrocarbons (IV) and (V) the electron cloud shifts in the same direction under the influence of substituents, yet water adds in a different way to the two compounds. For the unsymmetrically disubstituted acetylenes of type $CH_3-C\equiv C-R$, where $R = C_2H_5$, $CH(CH_3)_2$, and $C(CH_3)_3$, significantly non random addition is observed only in the last case, where a mixture of ketones, containing 65% of ethyl t-butyl ketone, is formed[333].

It seems that for all cases the sense of the addition is determined by the ease of formation and stability of the intermediate complex formed in the presence of the catalyst. It therefore depends on steric and other factors besides the polarisation of the initial molecule.

Alcohols are added to both multiple bonds of vinylacetylene in the presence of boron trifluoride and red mercuric oxide[334-336]:

$$HC\equiv C-CH=CH_2 \xrightarrow{ROH} CH_3-C(OR)_2-CH_2-CH_2-OR.$$

Glycols are added in the same way[337]. In the presence of alkali, different products are obtained, depending on the conditions[338,339]. In the presence of potassium alcoholate, at ordinary pressures, alcohols are added at 1,4-positions, yielding α-alkoxybutadienes, after isomerisation of the allene, formed initially to 1,3-diene[339,340].

$$HC\equiv C-CH=CH_2 \longrightarrow CH_2=C=CH-CH_2OR \longrightarrow CH_2=CH-CH=CH-OR.$$

β-Alkoxybutadienes, and, sometimes, acetylenic ethers are obtained as by-products in this reaction. If the reaction is carried out in the presence of sodium alcoholates, and under pressure, the 1,4-addition is followed by the isomerisation of the allenic ether first formed to an acetylenic ether[341]:

$$HC\equiv C-CH=CH_2 \xrightarrow{ROH} CH_2=C=CH-CH_2OR \longrightarrow CH_3-C\equiv C-CH_2-OR.$$

Addition of alcohols to vinylacetylene homologues containing a terminal ethynyl group proceeds in the same way as the addition of water[342,343]:

$$\underset{|\\CH_3}{HC\equiv C-C=CH_2} \xrightarrow{CH_3OH} \underset{|\\CH_3}{CH_3-C(OCH_3)_2-C=CH_2} \xrightarrow{CH_3OH} \underset{|\\CH_3}{CH_3-C(OCH_3)_2-CH-CH_2OCH_3}.$$

With cyclic conjugated enynes, the reaction is complicated by the formation of dimers of dienic ethers[344,345]. Enyne hydrocarbons with isolated multiple bonds add alcohols in the presence of $BF_3.HgO$ only to their acetylenic bond. The double bond does not react[346]. According to some authors vinylalkynes add alcohols in a similar manner in the presence of acid catalysts (boron trifluoride)[336,346]. However in the light of the latest results on the addition of water and alcohols to vinylalkynes in the presence of alcoholates, such claims need verifying. Vinylalkynes add alcohols (in the presence of sodium alcoholates) and water in an analogous manner[347]:

$$CH_3-C\equiv C-CH=CH_2 \xrightarrow{CH_3OH} CH_3-COCH_3=CH-CH=CH_2.$$

In the case of vinylethylacetylene a mixture of two ethers is formed, which on hydrolysis yields the same ethyl propenyl ketone[347]:

$$CH_3-CH_2-C\equiv C-CH=CH_2 \rightarrow$$

$$\rightarrow \begin{cases} CH_3-CH_2-COCH_3=CH-CH=CH_2 \\ \downarrow \\ CH_3-CH=COCH_3-CH=CH-CH_3 \end{cases} \rightarrow C_2H_5-CO-CH=CH-CH_3.$$

Allylacetylenes add alcohols similarly[346]:

$$R-C\equiv C-CH_2-CH=CH_2 \xrightarrow{ROH} R-C(OR)_2-CH_2-CH_2-CH=CH_2.$$

Acids unite with vinylacetylene to form β-acyloxybutadienes only, according to the scheme[348-350]

$$H-C\equiv C-CH=CH_2 \xrightarrow{RCOOH} CH_2=C(OCOR)-CH=CH_2.$$

In the presence of a catalyst based on boron trifluoride, 60% formyloxybutadiene, and 30% acetoxybutadiene are

formed. Poorer results are however obtained with mercuric sulphate. Benzoic acid did not react with vinylacetylene. A patent claims the preparation of β-phenoxybutadiene from vinylacetylene and phenol[351].

The behaviour of vinylacetylenic hydrocarbons in their reactions with water, alcohols, and hydrogen halides is of considerable interest to theoretical organic chemistry, particularly as regards the determination of the mechanism of Kucherov's reaction.

7. Addition of Sulphur, Nitrogen, Phosphorus, and Silicon Compounds

Vinylacetylene adds mercaptans to the double bond only and that in the opposite sense to Markownikoff's rule. It seems that a radical mechanism is operative in this reaction[352]:

$$HC\equiv C-CH=CH_2 \xrightarrow{CH_3C_6H_4SH} CH\equiv C-CH_2-CH_2SC_6H_4CH_3.$$

According to one patent[353] vinylacetylene reacts with hydrogen sulphide at 200° in the presence of Co_2S_3. Vinylacetylene adds thiocyanic acid at 50° in the presence of HgO giving thiocyanobutadiene[354]:

$$HC\equiv C-CH=CH_2 \xrightarrow{HSCN} CH_2=C(SCN)-CH=CH_2.$$

Vinylacetylene adds secondary amines at 1,4-positions, on heating under pressure in aqueous solution, yielding allenic amines; by prolonged heating with an excess of initial amine, or by the action of alcoholates, these are transformed into acetylenic amines[355]:

$$HC\equiv C-CH=CH_2 \xrightarrow{R_2NH} CH_2=C=CH-CH_2NR_2 \rightarrow CH_3-C\equiv C-CH_2NR_2.$$

It should be noted that diacetylene unites with amines even without heating[356], whereas this reaction is not characteristic of butadiene[357]. According to patents, vinylacetylene reacts with ammonia in the presence of a catalyst (Pb–Cd), yielding aliphatic amines as well as collidine and picoline[358]. Addition products are also formed with secondary amines – piperidine, morpholine, and methylaniline – in the presence of copper compounds[359].

Whereas amines do not react with vinylakynes on heating to 120° under pressure, they do react with analogous alcohols under such conditions. Allenic amino-alcohols are formed at first, but they are subsequently isomerised to aminoalkynols[360,361]. The addition products of amines with vinylacetylenic hydrocarbons can be obtained without heating by the recently discovered reaction of vinylacetylenic hydrocarbons with lithium dialkylamides. By treating with water the addition products of lithium dialkylamides with vinylacetylene, acetylenic amines are obtained. Such products obtained with vinylalkynes yield allenic amines on treatment with water[362].

$$HC\equiv C-CH=CH_2 \xrightarrow{R_2N-Li} H-C(Li)=C=CH-CH_2NR_2 \rightarrow Li-C\equiv C-CH_2-CH_2NR_2 \rightarrow$$
$$\xrightarrow{H_2O} HC\equiv C-CH_2-CH_2NR_2,$$

$$R-C\equiv C-CH=CH_2 \xrightarrow{R_2N-Li} R-CLi=C=CH-CH_2NR_2 \xrightarrow{H_2O} R-CH=C=CH-CH_2NR_2.$$

An exception is vinylmethylacetylene, which, under such reaction conditions mainly yields the dimer.

Similarly to lithium dialkylamides, lithium dialkylphosphides are added easily to vinylalkynes, yielding allenic phosphines[363]:

$$C_2H_5-C\equiv C-CH=CH_2 \xrightarrow{LiPR_2} C_2H_5-CLi=C=CH-CH_2PR_2 \xrightarrow{H_2O}$$
$$\rightarrow C_2H_5-CH=C=CH-CH_2PR_2.$$

In contrast to lithium phosphides, phosphorus tri- and pentachlorides react with the triple bond in vinylacetylene and its homologues[364–366]:

$$HC\equiv C-CH=CH_2 \xrightarrow{PCl_3,\ O_2} Cl_2PO-CH=CCl-CH=CH_2,$$

$$C_2H_5-C\equiv C-CH=CH_2 \xrightarrow{PCl_5} Cl_4P-\underset{\displaystyle C_2H_5}{\underset{|}{C}}=CCl-CH=CH_2 \xrightarrow{SO_2} Cl_2PO-\underset{\displaystyle C_2H_5}{\underset{|}{C}}=CCl-CH=CH_2.$$

In the reaction of vinylacetylene and isopropenylacetylene with phosphorus pentachloride simultaneous substitution of one of the hydrogen atoms by chlorine takes place[365].

Silanes also react with the vinylacetylene triple bond[367]. The catalyst for this interesting reaction is H_2PtCl_6.

$$HC\equiv C-CH=CH_2 \xrightarrow{Cl_2SiHR} Cl_2RSi-CH=CH-CH=CH_2.$$

8. Additions Resulting in the Lengthening of the Carbon Chain

Reactions belonging to this group are those with (a) acetylenes, (b) free radicals, (c) organolithium compounds, (d) halogen derivatives, (e) hydrocyanic acid, (f) nickel carbonyls, (g) dialkylcarbonates, and (h) diazo compounds.

(a) During its preparation from acetylene vinylacetylene can add another acetylene molecule and give ethynylbutadiene. At the same time the addition of vinylacetylene to acetylene takes place, forming divinylacetylene[368]:

$$HC\equiv C-CH=CH_2 \xrightarrow{HC\equiv CH} \begin{cases} HC\equiv C-CH=CH-CH=CH_2 \\ CH_2=C-C\equiv C-CH=CH_2. \end{cases}$$

(b) Triphenylchloromethane and mercury in benzene solution reacted for 12 days with vinylacetylene to yield apparently the 1,4-addition product of free triphenylmethyl radicals and vinylacetylene[369].

(c) Lithium alkyls and lithium aryls can react with vinylalkynes even at -60°. By treating the adducts with water, good yields of allenic hydrocarbons are obtained[370–372]:

$$CH_3-C\equiv C-CH=CH_2 \xrightarrow{C_4H_9-Li} CH_3-CLi=C=CH-CH_2-C_4H_9 \xrightarrow{H_2O}$$
$$\rightarrow CH_3-CH=C=CH-CH_2-C_4H_9.$$

Large yields of allenic hydrocarbons in this reaction seem to be connected with the low reactivity of intermediate addition products, containing lithium attached to the double bond.

(d) In the presence of Gustavson's catalysts vinylacetylene and its homologues containing a terminal ethynyl group add tertiary halogen derivatives to their triple bond[373,374]:

$$HC\equiv C-CH=CH_2 \xrightarrow{R_3C-Cl} R_3C-CH=CCl-CH=CH_2.$$

Under the same reaction conditions vinylalkynes yield primarily allenic adducts, radical adding to the double bond[375]:

$$R{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{R_3C-Cl} R{-}CCl{=}C{=}CH{-}CH_2{-}CR_3.$$

Thus, only in the first case is the sense of the addition of halogen derivatives identical with that of hydrogen halides in the presence of catalysts.

Vinylacetylene adds α-chloro-ethers in the presence of $BiCl_3$, primarily at 1,4-position. However, the primary addition products can be isomerised to compounds with conjugated multiple bonds[376]:

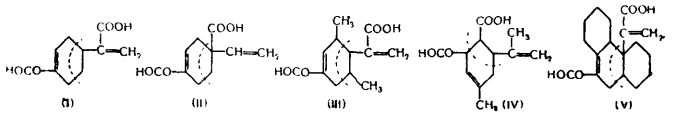
$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{ROCH_2Cl} \begin{cases} RO{-}CH_2{-}CH{=}C{=}CH{-}CH_2Cl \\ RO{-}CH_2{-}CH{=}CCl{-}CH{=}CH_2. \end{cases}$$

Acid chlorides unite with vinylacetylene giving dienic β-chloro-ketones[377].

(e) The reaction of vinylacetylene with hydrocyanic acid has only been described in one patent, which claims that the reaction at 50°, in the presence of copper powder, yields 1-cyanobuta-1,3-diene[378]:

$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{HCN} NC{-}CH{=}CH{-}CH{=}CH_2.$$

(f) Of considerable interest is the reaction of vinylacetylene and its homologues with nickel carbonyls. This yields the dimers of the expected 1,3-dienoic acids. Reactions of nickel carbonyl with vinylpropenyl-, isopropenyl- and cyclohexenyl acetylenes have been studied[379-382]. There are contradictions among the available data regarding the structure of the intermediate 1,3-dienoic acids and the course of their dimerisation. Intermediate dienoic acids were attributed formulae of the type R–CH = CR'–CH = CH–COOH or R–CH = CR'–C(COOH) = CH_2. Authors who agree on the structure of dienoic acids nevertheless have different views on the dimerisation mechanism. For instance, two formulae, (I) and (II), were suggested for the dimeric acid from vinylacetylene[381,382]. Formula (II) seems to be better justified, having been verified by synthesis[381]. Acids prepared from propenyl-, isopropenyl- and cyclohexenylacetylenes were given formulae (III), (IV), and (V):



Further study is needed to determine conclusively the structure of all these adducts.

(g) By prolonged heating of isopropenylacetylene with diethyl carbonate in the presence of sodium alcoholate, addition to the triple bond takes place[383]:

$$HC{\equiv}C{-}C(CH_3){=}CH_2 \xrightarrow{(C_2H_5O)_2CO} \begin{cases} C_2H_5OCO{-}CH_2{-}C(OC_2H_5)_2{-}C(CH_3){=}CH_2 \\ C_2H_5OCO{-}CH{=}COC_2H_5{-}C(CH_3){=}CH_2. \end{cases}$$

(h) Diazomethane reacts with the triple bond in vinylacetylene yielding ethynylpyrazoline[384].

$$HC{\equiv}C{-}CH{=}CH_2 + CH_2N_2 \rightarrow HC{\equiv}C{-}C(=N{-}NH){-}CH_2.$$

Dombrovskii has shown that aromatic diazonium halides halogenate and arylate the vinylacetylene double bond[385-387]:

$$HC{\equiv}C{-}CH{=}CH_2 \xrightarrow{C_6H_5N_2Cl} HC{\equiv}C{-}CHCl{-}CH_2{-}C_6H_5.$$

Considerable quantities of allenic chlorides (1,4-addition[388]) are also formed in the reaction.

9. Isomerisation with Rearrangement of the Multiple Bonds

Several cases have been described of isomerisation by multiple bond migration during the preparation of enyne hydrocarbons. Such isomerisation may result in the formation of a conjugated system from the non-conjugated one, as, for instance, in the case of allylacetylene formed in the reaction of allyl bromide with sodium acetylide[167]. In other cases the migration of the entire system of multiple bonds takes place. For example, an excess of sodium amide causes the isomerisation of methylisopropenylacetylene during its preparation according to the scheme[180]

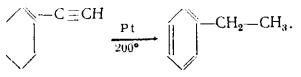
$$NaC{\equiv}C{-}C(CH_3){=}CH_2 \xrightarrow{CH_3Br} CH_3{-}C{\equiv}C{-}C(CH_3){=}CH_2 \xrightarrow{NaNH_2} HC{\equiv}C{-}CH{=}C(CH_3)_2.$$

When the reaction can yield two types of vinylacetylenes, namely R–C ≡ C–CH = CH_2 and R–CH = CH–C ≡ CH, the first compound usually predominates[20,22].

Multiple bond migration is observed in brominating allylbutylacetylene with bromosuccinimide[389]:

$$C_4H_9{-}C{\equiv}C{-}CH_2{-}CH{=}CH_2 \longrightarrow C_4H_9{-}C{\equiv}C{-}CH{=}CH{-}CH_2Br.$$

Irreversible (Zelinskii') catalytic conversion is characteristic of alicyclic vinylacetylenes[390]

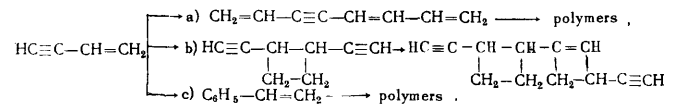


10. Dimerisation and Polymerisation of Vinylacetylene and its Homologues

Condensation reactions, characteristic of dienic hydrocarbons, can proceed in two ways — to form cyclic six-membered dimers, or linear polymers[356]. Vinylacetylenic hydrocarbons have a very small tendency to form six-membered rings. By dimerisation, they yield compounds containing four-membered rings[391]

Polymerisation of vinylacetylene at moderate temperatures and pressures can take three different paths, depending on the conditions, and yield (a) a linear dimer and its polymers, (b) a dimer with a four-membered ring and its

polymers, and (c) styrene and its polymers[1,391]:



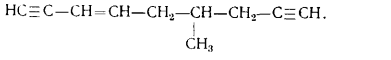
Linear dimerisation of vinylacetylene occurs under the action of the CuCl.NH_4Cl complex. The reaction mechanism is analogous to that for the formation of vinylacetylene[395]. Heating vinylacetylene without a catalyst at 105° yields a mixture of products containing 1% of dimer, 3% of trimer, 16% of tetramer, 8% of pentamer, and 72% of higher polymers. All the products contain four-membered rings[391].

Polymerisation of vinylacetylene to styrene is catalysed by organic acids. For instance, in the presence of acetic acid the yield of styrene can reach 50% of the reacted vinylacetylene[391]. Attempts have been made to determine the rate of dimerisation of vinylacetylene[396].

Slobodin studied the copolymerisation of vinylacetylene with SO_2. In the absence of water a polymer of the composition $(C_4H_4.SO_2)_x$ is formed, insoluble in water and organic solvents. In the presence of water the polymer has the composition $(C_4H_4.SO_3)_x$. In contrast to the case with butadiene sulphone monomer is not obtained in this reaction[397].

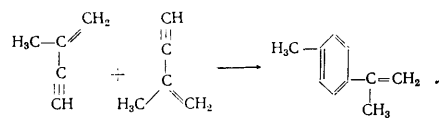
Possible preparations of valuable products, by copolymerisation of vinylacetylene, especially with dienes, have been covered by a number of patents[142,398-406]. The addition of vinylacetylene does not affect the rate of emulsion polymerisation of butadiene, but it does promote the cross-linking of chains in rubber, thus lowering its solubility and tensile strength. Vinylacetylene inhibits the polymerisation of butadiene by alkali metals[407]. The presence of small quantities of vinylacetylene in butadiene has a considerable effect on the toughness of butadiene-styrene rubbers[480]. Vinylacetylene does not affect the induction period of the polymerisation of vinylacetate in the presence of peroxides, but it somewhat inhibits the process[409]. It also retards the polymerisation of chloroprene and causes brittleness of the polymer[410]. Vinylacetylenes are recommended for stabilising chlorinated hydrocarbons and other products[411,412].

The polymerisation of vinylacetylene homologues has received even less attention. Linear dimerisation was only observed in the reaction of vinylmethylacetylene with lithium dialkylamides. The dimer obtained was shown to have the following structure[362]:



It seems that in this reaction lithium methylvinylacetylene, first formed by substituting a hydrogen atom in methylvinylacetylene, subsequently combines with the original hydrocarbon.

Prolonged heating of isoalkenylacetylenes in alcoholic solution, especially in the presence of acetic acid, yields dimers with six-membered rings. The structure of the main fraction of the dimers was established by oxidation to the corresponding aromatic acids[58,74,413]:

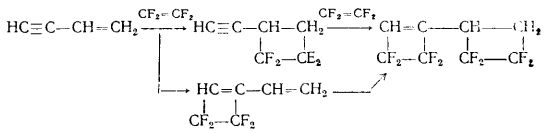


Analogous dimers are often formed during the dehydration of dialkylpropargyl alcohols. The presence of branched radicals at the terminal carbon of the double bond favours dimerisation[74]. In some cases the formation of dimers with eight-membered rings was observed. There are patents on the polymerisation of vinylmethyl- and isopropenylacetylene[414-416].

Heating at 300° for 24 h transforms vinylacetylene in 94% yield to a yellow powder, which chars above 300°[392]. At 25° and 6000 atm 50% of vinylacetylene polymerises in 350 h, and of butadiene in 280 h[393]. Heating vinylacetylene to 345°–355° with copper oxide yields a cuprenelike product[394]. Polymerisation to a solid product is also observed on irradiation by α-rays from radon[188]. Copolymerisation of isopropenylacetylene with SO_2 yielded similar products to those obtained from vinylacetylene[397].

11. Addition of Fluoroolefines.

Vinylacetylene reacts at 100° with tetrafluoroethylene forming cyclobutane and cyclobutene derivatives[417]:



12. Formation of Complexes

Very little is known of the reactions of vinylacetylenic hydrocarbons with the the salts of heavy metals with the exception of copper salts.

Solid cuprous chloride absorbs vinylacetylene; 1 g of salt absorbs 128 cm^3 of vinylacetylene, compared with 74 cm^3 of acetylene and 10 cm^3 of ethylene.

In solution vinylacetylene forms a complex with CuCl.NH_4Cl with the composition $C_4H_4.Cu_2Cl_2.NH_4Cl$.

In hydrochloric acid solution of CuCl the composition of the complexes formed depends on the acid concentration, e.g. CuCl.C_4H_4 (10% HCl) and 2CuCl.C_4H_4 (20% HCl). Dry HCl displaces vinylacetylene in the above complexes and the complex $C_4H_4.4CuCl.HCl$ is formed[420,421].

Vinylacetylene can displace carbon monoxide in cobalt carbonyl $Co_2(CO)_8$. With isopropenylacetylene, this carbonyl forms reddish brown crystals of composition $C_5H_8.Co_2(CO)_6$[422]. Complexes are probably also formed in the reaction of acetylenes and vinylacetylenes with palladium salts[423].

B. REACTIONS INVOLVING ACETYLENIC HYDROGEN

Metals, halogens, and, particularly, hydrocarbon radicals can be substituted for the acetylenic hydrogen in enyne hydrocarbons containing a terminal ethynyl group.

1. Substitution of Acetylenic Hydrogen by Halogens

Substitution of the acetylenic hydrogen by halogens takes place on passing vinylacetylene and its homologues containing a terminal ethynyl group through solutions of alkali

hypohalogenites. Chloro-, bromo-, and iodo-derivatives of vinyl-, propenyl-, and isopropenylacetylenes were prepared in this way[424-427]. They can also be prepared by dehydration of the corresponding tertiary acetylenic alcohols in the presence of formic acid[428].

$$HC\equiv C-CH=CH_2 \xrightarrow{NaOCl} Cl-C\equiv C-CH=CH_2$$

$$Cl-C\equiv C-\underset{\underset{CH_3}{|}}{COH}-CH_3 \xrightarrow{-H_2O} Cl-C\equiv C-\underset{\underset{CH_3}{|}}{C}=CH_2$$

Small quantities of acetylenic halides are also formed by the dehalogenation of vinylacetylenic dihalides[429]. Acetylenic halides have the interesting property of yielding unsaturated acids by reaction with alcoholic alkalis[430]:

$$R-CH=CR-C\equiv CCl \longrightarrow R'RC=CH-COOH.$$

2. Substitution of Acetylenic Hydrogen by Metals and Non-Metals

Vinylacetylenic hydrocarbons with a terminal ethynyl group have relatively labile ("acid") hydrogen atoms[431]. A study was made of the kinetics of the reaction of monosubstituted acetylenes with C_2H_5MgBr. If the reaction rate with butylacetylene is 100, that with isopropenylacetylene[432] is 40.

All alkenylacetylenes form the corresponding acetylides by the action of alkali amides in liquid ammonia. On reaction with solutions of organomagnesium compounds they displace saturated hydrocarbons yielding halogenomagnesiumacetylides, soluble in ether[433]. On treatment with alkaline solutions of silver and monovalent copper salts they form explosive acetylides[2,9,11,12,317,434,435], sometimes as double salts with those with which they reacted[11,12,434].

Crystalline mercury vinylacetylides have also been described[100,153,436,437]. Mercury bis(vinylacetylide) is formed in the reaction of vinylacetylene with alkaline solutions of K_2HgI_4 or mercuric acetate. At 60°–70° a product of the composition $C_{10}H_{12}O_7Hg_3$ is formed. Mercury derivatives can be used for separating and identifying geometrical isomers of vinylacetylenic hydrocarbons[100].

Organosilicon compounds containing vinylacetylenic radicals have been prepared by reacting alkylhalogenosilanes with bromomagnesiumvinylacetylides[438-440]:

$$R_3Si-Cl + BrMg-C\equiv C-CH=CH_2 \rightarrow R_3Si-C\equiv C-CH=CH_2.$$

Tin vinylacetylides were recently prepared by this method[441]:

$$R_3Sn-Cl + BrMg-C\equiv C-CH=CH_2 \rightarrow R_3Sn-C\equiv C-CH=CH_2.$$

3. Condensation with Carbonyl Compounds *

Vinylacetylene and its homologues containing a terminal ethynyl group can easily be condensed with various aldehydes, ketones, epoxides, acid anhydrides, and CO_2.

The reaction with formaldehyde can be carried out either by the Grignard-Iotsich method using vinylacetylene Grignard reagents[60,102,442] or by Reppe's method[443]:

$$HC\equiv C-CH=CH_2 + CH_2O \xrightarrow{[Cu(OCOH)_2]} CH_2OH-C\equiv C-CH=CH_2.$$

With other aldehydes, in addition to these two methods[444-446], condensations can also be carried out with sodium acetylide in liquid ammonia[447,448]. With unsaturated aldehydes, best results are obtained by using organomagnesium compounds[448,449].

Condensations of enyne hydrocarbons with ketones proceed easily by the Grignard-Iotsich reaction, using sodium amide in liquid ammonia or finely dispersed KOH in ether (Favorskii's method)[447,450-454]. Good results are obtained in condensations of vinylacetylenes or their metal derivatives in the presence of powdered KOH (according to Favorskii) with cyclic ketones[452,455-461], unsaturated ketones[462,463], hydroxy-[459], alkoxy-[464-466], and amino-ketones[467]. Nazarov and his collaborators carried out a large number of such condensations. Of special interest in this field is the condensation of isopropenylacetylene with β-ionone, as a step in the synthesis of carotenoid compounds[55,468,469]

In the reaction with epoxides halogenomagnesiumvinylacetylides yield primary alcohols[445]:

$$H_2C\underset{\diagdown O \diagup}{-}CH_2 + BrMg-C\equiv C-CH=CH_2 \longrightarrow CH_2OH-CH_2-C\equiv C-CH=CH_2.$$

With ethyl acetate, a tertiary alcohol containing two vinylacetylenic radicals[469] is formed:

$$CH_3-CO-OC_2H_5 + 2BrMg-C\equiv C-CH=CH_2 \longrightarrow CH_3-C(OH)(C\equiv C-CH=CH_2)_2.$$

Vinylacetylides react with acetic and other anhydrides yielding vinylacetylenic ketones[58,89,104,470].

$$(CH_3-CO)_2O + BrMg-C\equiv C-CH=CH_2 \rightarrow CH_3-CO-C\equiv C-CH=CH_2.$$

With carbon dioxide, sodium and magnesium derivatives of acetylene form enynoic acids, usually isolated as esters[371,471-473].

$$CO_2 + BrMg-C\equiv C-CH=CH_2 \rightarrow HO-CO-C\equiv C-CH=CH_2.$$

Heating vinylacetylene with paraformaldehyde and secondary amines results in the Michael condensation. This reaction is catalysed by ferric chloride[474,475]:

$$CH_2=CH-C\equiv CH + CH_2O + HNR_2 \rightarrow CH_2=CH-C\equiv C-CH_2NR_2.$$

4. Oxidative Condensation

In Section I the oxidative dimerisation of vinylacetylenes containing a terminal ethynyl group was considered. Similar oxidative condensation is possible between enyne hydrocarbons and other acetylenic compounds. Condensation of enynes with acetylenic acids has been used for the synthesis of natural higher unsaturated acids, for instance, erythrogenic acid[103,171]:

$$CH_2=CH(CH_2)_4-C\equiv CH + HC\equiv C-(CH_2)_7-COOH \xrightarrow{O_2,\ CuCl,\ NH_4Cl}$$

$$\rightarrow CH_2=CH-(CH_2)_4-C\equiv C-C\equiv C-(CH_2)_7-COOH.$$

* Vartanyan and his coworkers have recently shown that vinylacetylene can be condensed with aldehydes in the presence of KOH, provided the reaction is carried out without a solvent at very low temperatures[475].

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MOLECULAR SIEVES — PREPARATION, PROPERTIES, AND APPLICATIONS

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INTRODUCTION

The sorptive properties of sorbents depend chiefly on the area and chemical nature of the surface, the pore structure, and the distribution of effective pore radius.

The adsorption potential, which determines the amount of adsorption, can vary greatly with change in the geometrical shape of the internal surface; it is much greater in narrow pores and channels of molecular dimensions, owing to the superposition of the fields of the opposite walls, and this effect is more marked the finer the pores of the adsorbent[1]. The free adsorptive surface of an adsorbent also depends on the dimensions of the molecules of the substance being adsorbed, since some of the finest pores may be inaccessible to large molecules. This leads to the so-called ultraporosity effect.

Some sorbents are known to have pore diameters approximately equal to molecular dimensions. Only very small molecules can penetrate into these fine pores. McBain has called this phenomenon "persorption"[2].

Fine pores are also present in activated charcoal, silica gel, and other technical sorbents, so that each shows the ultraporosity effect to some extent. The surface area cal-