RUSSIAN CHEMICAL REVIEWS
Uspekhi Khimii

May 1964

U.D.C. 547.311 : 547.312

ADVANCES IN THE CHEMISTRY OF DIVINYLACETYLENE

S. A. Vartanyan

CONTENTS

1. Introduction 243
2. Synthesis of divinylacetylene and its homologues 243
3. Polymerisation of divinylacetylene 244
4. Hydrogenation 245
5. Addition of halogens 245
6. Addition of thiophenols 246
7. Addition of alcohols 246
8. Addition of amines 246
9. Addition of lithium alkyls 246
10. Addition of ROX, $ROCH_2Cl$, and $C_6H_5N_2Cl$ 246
11. Addition of hydrogen halides 247
12. Oxidation of divinylacetylene hydrocarbons 248
13. Cyclisation 248
14. Cyclohydration 249
15. Synthesis of β-alkoxyketones by hydration of divinylacetylene hydrocarbons in aqueous solutions of alcohols 250
16. Alkylation and cycloalkylation 254
17. Diene synthesis 254
18. Aldehydes and glycols of the divinylacetylene series 255

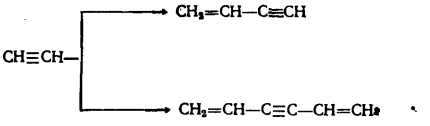
1. INTRODUCTION

Intense research into the chemistry of acetylene and its derivatives has led to the possibility of their preparation from many compounds which are nowadays used on an industrial scale as intermediate products. However, the great tendency of divinylacetylene and its homologues to polymerise and the danger of explosion of these polymers have until now retarded the development of the chemistry of divinylacetylene, despite the fact that divinylacetylene is very reactive, as a result of the presence of one triple and two double bonds, and constitutes an interesting raw material for organic synthesis. The numerous and various reactions of these compounds even at this stage suggest the possible ways of their utilisation in chemistry.

The advances in the chemistry of divinylacetylene have not been reviewed, except for Nazarov's article[1] which deals only with the mechanism of the hydration and cyclisation of dienynes. In the present review an attempt is made to collect, and as far as possible arrange in a systematic manner, the extensive data on this problem which are at present available.

2. SYNTHESIS OF DIVINYLACETYLENE AND ITS HOMOLOGUES

Mignonac and de Saint-Aunay[2] showed that, when acetylene is subjected to high frequency discharges at -60°, vinylacetylene and divinylacetylene (DVA) are formed. The authors explained the formation of DVA by postulating the addition of acetylene to vinylacetylene. The polymerisation of acetylene into vinylacetylene, DVA, and higher polymers under the action of concentrated aqueous solutions of cuprous chloride and ammonium chloride, discovered by Nieuwland and coworkers[3] in 1931, is of considerable importance for the synthesis of DVA:



Basically, the numerous studies on the synthesis of DVA are various modifications of Nieuwland's work[3]. Taking the available results as a whole, we can divide these syntheses into the following groups (bearing in mind the composition of the catalyst, the conditions, and the reaction medium): the use of Nieuwland's catalyst with modified concentrations of its various components[4-19]; replacement of ammonium chloride by other substances[6,7]; the use of anhydrous solvents[18-33], dispersing agents[24,25], carriers[26], high temperature[27-31], and acetylene under pressure[32].

In all cases DVA is formed together with vinylacetylene. By controlling the reaction conditions, preferential formation of either monovinylacetylene or DVA and higher polymers can be achieved. It has been established that increase of the reaction temperature and of the concentration of cuprous chloride lead to higher amounts of DVA. One of the patents of the Nippon Mining Company[33] indicates that acetylene can be polymerised to give a 100% yield of the trimer, *i.e.* DVA.

In the laboratory DVA can be prepared by the action of the magnesium bromide derivative of vinylacetylene or acetaldehyde followed by dehydration of the resulting methylvinylethynylmethanol[34]:

$$CH_3CHO + BrMgC{\equiv}C{-}CH{=}CH_2 \rightarrow CH_3{-}\underset{OH}{CH}{-}C{\equiv}C{-}CH{=}CH_2 \xrightarrow{-H_2O} CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 .$$

Divinylacetylene can also be obtained by the action of the di(magnesium bromide) derivative of acetylene on 1,2-dichloro-2-ethoxyethane followed by the splitting off of the ethoxy-group and the chlorine, by treatment with zinc, from the acetylene dichloride formed[35]:

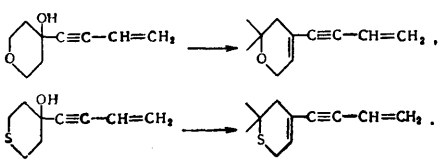
$$2\,CH_2{-}CHCl + BrMgC{\equiv}CMgBr \rightarrow CH_2{-}\underset{Cl}{CH}{-}C{\equiv}C{-}\underset{OC_2H_5}{CH}{-}CH_2{-}Cl \xrightarrow{-C_2H_5Cl} CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2 .$$

Iotsich[36] obtained 1,1,6,6-tetrachlorodivinylacetylene by the action of zinc on the acetate of the acetylene glycol derived from chloral:

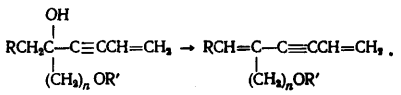
$$CCl_3{-}\underset{OCOCH_3}{CH}{-}C{\equiv}C{-}\underset{OCOCH_3}{CH}{-}CCl_3 \rightarrow CCl_2{=}CH{-}C{\equiv}C{-}CH{=}CCl_2 .$$

Apart from the first representative of the divinylacetylene hydrocarbons, DVA itself, which is mainly obtained by polymerisation of acetylene, substituted divinylacetylenes are prepared by dehydration of vinylacetylene alcohols and acetylene glycols. As a result of Nazarov's work, vinylacetylene alcohols are readily available. Dehydration of these alcohols yields a series of divinylacetylenes containing one substituted vinyl group[37]. It has been established[37-47] that tertiary vinylacetylene alcohols readily split off water on heating with practically all the dehydrating agents — sulphuric, phosphoric, acetic, formic, *p*-toluenesulphonic acids, acetic anhydride, etc.

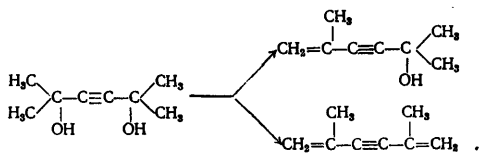
In practice the most convenient method of dehydrating vinylethynylmethanols is heating with 50–60% sulphuric acid; the yield of the corresponding dienyne then amounts to 70–90%. This method of dehydration makes it possible to synthesise also divinylacetylene compounds in which one vinyl group is linked to a heterocyclic ring[40,41,47]:



Dehydration of α- and β-alkoxyvinylacetylene alcohols takes place similarly[43-46]:



When acetylene 1,4-glycols are shaken with 20–40% sulphuric acid and heated on a water-bath, two molecules of water are split off and divinylacetylene hydrocarbons are obtained[48-56]. This is one of the convenient methods of synthesising dienynes. Dupont[52] established that dehydration of acetylene glycols takes place in two stages with the formation of substituted vinylacetylene alcohols which then lose yet another molecule of water and the corresponding dienyne is obtained:



Phosphoric acid (60%) has also been used for this purpose[50]. Other workers have also used potassium hydrogen sulphate as dehydrating agent[57-60]. Zalkind and Shuvalov[60] used sodium instead of potassium hydrogen sulphate at 150°. Marvel[49] and Babayan[61] showed that acetylene glycols are smoothly dehydrated under the action of *p*-toluenesulphonic acid at 140–150°, the yields of dienynes reaching 90%. Petrov and Korlik[62] established that oxalic acid can also be employed for the dehydration of acetylene glycols. Krestinskii and Summ[63] showed that tetraethylbutyne-1,4-diol is dehydrated on being shaken with formic acid, the expected dienyne being formed in almost theoretical yield.

However, it must be noted that on dehydration of vinylacetylene alcohols and acetylene glycols it is not always possible to isolate the expected dienyne, because under the reaction conditions side-reactions occur. Sometimes under the dehydration conditions the dienynes undergo direct cyclohydration with the formation of cyclic ketones[49]. The Meyer–Schuster rearrangement[64] also frequently occurs, and also cyclohydration of the glycols into the corresponding furandiones[65]. Recently a continuous method of synthesising divinylacetylene hydrocarbons, by vapour-phase dehydration of vinylacetylene alcohols over aluminium oxide at 150–400°, has been developed. An industrial process for the manufacture of vinylisopropenylacetylene has been proposed[66].

3. POLYMERISATION OF DIVINYLACETYLENE

DVA is a colourless liquid which rapidly becomes yellow on standing without a stabiliser; b.p. 85°/680 mm; n_D^{20} = = 1.5047; d_4^{20} = 0.7759.[67] On being kept in air, it absorbs oxygen, forming peroxy-compounds, and polymerises into a brittle polymer which readily explodes as a result of mechanical action — impact, friction, or heating. On heating the polymerisation of DVA is greatly accelerated. To prevent the formation of the peroxy-compounds, experiments on the polymerisation of DVA must be carried out either in the presence of a stabiliser or in an atmosphere of an inert gas[68]. The first stage of the polymerisation then yields a viscous product of an amber colour which gradually thickens and is converted into a brittle infusible and non-explosive mass[69]. The latter does not dissolve in organic solvents, is very stable to acids, alkalis, chlorine,

and bromine, and has therefore been suggested as a coating for various surfaces[69,70]. Morozov[71] suggested that the surface of electrodes used in the electrolysis of alkali metal chlorides should be impregnated with the DVA polymer. In the presence of anti-oxidants (pyrogallol, hydroquinone, α-naphthol, etc.) DVA can be kept in a closed vessel for about a year. On longer storage, it becomes yellow and polymerises. According to the literature, the intermediate liquid DVA polymers possess the properties of rapidly drying oils[71-83]. Their solutions in butyl acetate and other solvents yield satisfactory stable films on drying. Copolymers of propene and pentene with DVA and vinylacetylene, obtained in the presence of catalysts, can be used for coating metallic and glass surfaces. On heating with sulphur dichloride, DVA is converted into a resin or a liquid mass which is also suitable for coating metals[84].

Products with the properties of drying oils are also obtained on reaction of DVA with hydrogen polysulphide. The liquid polymers thus formed are recommended for the preparation of films, varnishes, and for various coatings[85]. Other workers have used hydrogen sulphide and sulphur; the reaction was carried out under pressure in the presence of dibutylamine, pyridine, sodium hydroxide, and ammonia[86].

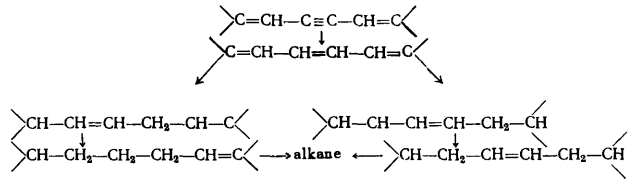
Drying oils are also obtained when chlorine is allowed to act upon the liquid polymers of DVA.[87] Despite the fact that the films and varnishes obtained from DVA age rapidly and become brittle, they have been recommended for use as drying oils[71], adhesives for rubber and metals[87], additives to Diesel fuel[88] and lubricating oils[89], and also as plasticisers for natural rubber[90,91]. In the presence of sodium naphthenate and gelatin DVA polymerises into a rubberlike product[92]. On heating for 10 h at 90°, divinylacetylene is converted into a mixture of dimer and trimer. Carothers distilled the dimer under a high vacuum and established that its molecular weight is 156, which corresponds to the formula $C_{12}H_{12}$. On bromination the dimers yield octa- and deca-bromides, on hydrogenation they absorb twelve hydrogen atoms, and on oxidation they are converted into *trans*-cyclobutane-1,2-dicarboxylic acid[93]. According to Carothers, the dimer has the structure of *trans*-1,2-di(vinylethynyl)cyclobutane and the trimer of di(vinylethynylcyclobutyl)acetylene.

Substitution of the hydrogen atoms of divinylacetylene by various radicals (aliphatic, alicyclic) enhances its stability to polymerisation. The substitution of the terminal hydrogen atoms has a particularly great inhibiting effect on polymerisation. Tetra-substituted divinylacetylenes polymerise either very slowly or not at all. As a result of the conjugated system of two double and one triple bond, they exhibit high elevation of molecular refraction (up to 5–6 units).

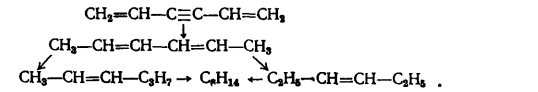
Like divinylacetylene itself, mono- or di-substituted divinylacetylenes thicken on standing, are converted into a viscous jelly, and finally into a solid mass of orange colour. On the walls of the vessel they form characteristic solid peroxy-compounds which explode on impact or friction. In a thin layer divinylacetylene polymerises in the course of several hours into a solid film.

4. HYDROGENATION

Blomquist and Marvel[48] were the first to show that divinylacetylene hydrocarbons are completely hydrogenated in the presence of a platinum catalyst with the formation of the corresponding saturated hydrocarbons. It was then established that, depending on the nature of the catalyst and on the method of its preparation, the hydrogenation of DVA and also its homologues takes place more vigorously when they are freshly distilled. In the presence of a palladium catalyst the hydrogenation stops after absorption of six hydrogen atoms (instead of the expected eight), whereas in the presence of a platinum catalyst eight hydrogen atoms are absorbed and the corresponding saturated hydrocarbon is formed. Some workers[48,53] believe that the first molecule of hydrogen adds to the triple bond with the formation of a 1,3,5-triene; the second hydrogen molecule can add on to the 2- or 4-positions. In the presence of a platinum catalyst a saturated hydrocarbon is then formed and in the presence of palladium an olefin:

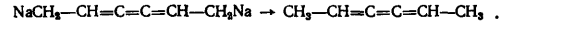


The hydrogenation of divinylacetylene itself was studied by many workers[94-99]. According to the data of Komada[96], the product is hex-3-ene and according to Katake[97] hex-2-ene. Isagulyants and coworkers[99] studied the hydrogenation of DVA in solution in ethanol, acetic acid, and xylene at the normal pressure or under a high pressure of hydrogen in the presence of a nickel catalyst. They established that the product is hexa-2,4-diene, whose formation is explained by the double addition of hydrogen to the 1- and 4-positions; further hydrogenation of hexa-2,4-diene yields hex-2-ene, hex-3-ene, and also hexane:



Klebanskii[94], who used palladium deposited on barium sulphate as the catalyst, established that the hydrogenation of DVA stops at the triene stage. Other workers showed that in the presence of platinum or nickel catalysts dienynes are hydrogenated to the corresponding saturated hydrocarbons. According to these workers, the reaction proceeds *via* the formation of 1,3-diene.

When divinylacetylene is reduced with sodium amalgam[94], hydrogen adds on to the 1- and 6-positions with the formation of 2,3,4-hexatriene:

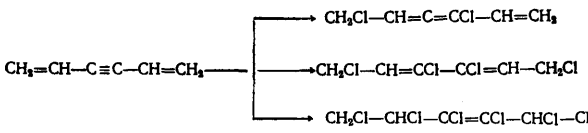


Klebanskii explains the addition of metal atoms to the 1- and 6-positions by the fact that the acetylene bond in the divinylacetylene molecule increases the electron density at the terminal atoms. When divinylacetylene is hydrogenated under a pressure of 10 atm in the presence of catalysts, the product is a mixture of hexenes, hexadienes, and hexatrienes, which can be used as rapidly drying oils[82]. Drying oils are also obtained on hydropolymerisation of DVA.[82]

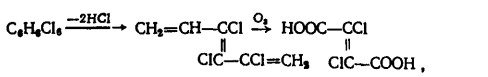
5. ADDITION OF HALOGENS

Chlorination of divinylacetylene[100] yielded di- and tetra-chlorides and also crystalline hexachlorohex-3-ene which

has the odour of camphor and is formed as a result of successive addition of chlorine to divinylacetylene to the 1- and 4-positions:

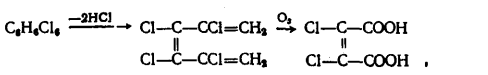


Two isomers of 1,2,3,4,5,6-hexachlorohex-3-ene were isolated. The structure of these hexachlorides was established by splitting off two molecules of hydrogen chloride in both isomers and subsequent ozonolysis [101]. Ozonolysis of the tetrachlorohexatriene obtained from the isomer with m.p. 59° yielded dichlorofumaric acid. On this basis, a *trans*-configuration was assigned to the initial hexachlorohex-3-ene:



m.p. 59°.

Ozonolysis of the tetrachlorohexatriene obtained from the isomer with m.p. 91° gave dichloromaleic acid, and therefore the isomer has the *cis*-configuration:

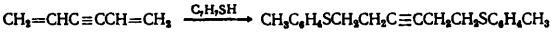


m.p. 91°.

Bromine adds to divinylacetylene similarly, with the formation of two stereoisomeric hexabromides [3,34,102]. The bromination takes place so smoothly that some workers use this reaction for the identification of divinylacetylene [3,34].

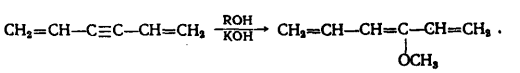
6. ADDITION OF THIOPHENOLS

Thiocresol adds on to divinylacetylene at the 1- and 2-positions (with respect to the vinyl groups) with the formation of 1,6-di-*p*-tolylthiohex-3-yne, which on oxidation with permanganate in acetone yields β-*p*-tolylsulphonylpropionic acid [103]:



7. ADDITION OF ALCOHOLS

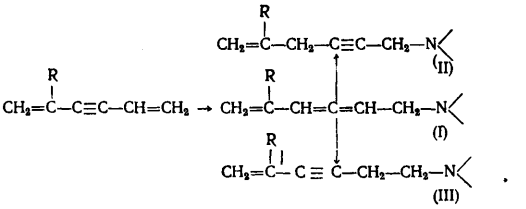
Dry methanol does not add to DVA under the action of a mercury catalyst [104,105], but there are data which suggest that the addition occurs at the 1- and 4-positions on heating in the presence of sodium alkoxide [106-108]. When divinylacetylene is boiled in methanol in the presence of sodium alkoxide for 40-60 h, 3-methoxyhexa-1,3,5-triene is formed in small yield [105-108]:



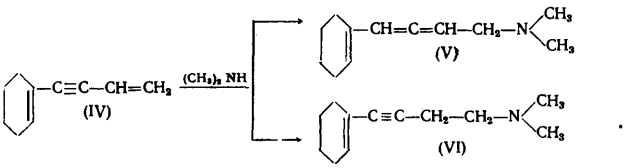
According to Klebanskii's data, under these conditions ethanol adds to divinylacetylene at the 1- and 6-positions [107,108]. Klebanskii also achieved the addition of ethanol to divinylacetylene on boiling in the presence of alkali and showed that under these conditions the addition also takes place at the 1- and 6-positions. It is possible that the mode of addition of alcohols depends on the alkyl radical. Methanol adds on to the 1- and 4- and ethanol to the 1- and 6-positions [106,107].

8. ADDITION OF AMINES

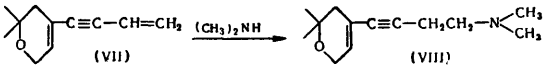
In order to synthesise amines derived from vinylacetylene, Vartanyan and Badanyan [109] studied the addition of amines to divinylacetylene hydrocarbons. They found that, when a mixture of an aqueous solution of dimethylamine and dienyne is heated in a sealed tube at 95-100° (40 h), one molecule of the amine adds to the dienyne at the 1- and 4-positions, so that the amino-group becomes attached to the terminal carbon atom of the substituted vinyl group; the resulting trienynylamine (I) undergoes two types of isomerisation under the reaction conditions, amines derived from allylacetylene (II) and vinylacetylene (III) being formed:



The structure of the amines was demonstrated by oxidation, hydrogenation, and synthesis. A study has also been made of the addition of amines to divinylacetylene systems in which one vinyl group is present in an alicyclic or tetrahydropyran ring. It was shown that under these conditions dimethylamine adds to Δ^1-cyclohexenylvinylacetylene (IV), also with the formation of amines derived from allene (V) and acetylene (VI):

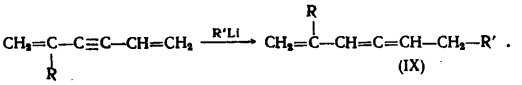


The addition of dimethylamine to the dienyne (VII) takes place similarly, but in this case only the expected aminoalkylacetylene (VIII) [110] is obtained in good yield:



9. ADDITION OF LITHIUM ALKYLS

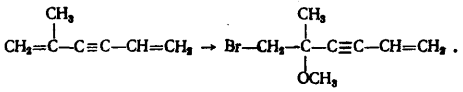
It has been established that lithium alkyls add on to divinylacetylene hydrocarbons at the 1- and 4-positions on the side of the unsubstituted vinyl group [111], triene hydrocarbons (IX) being obtained:



10. ADDITION OF ROX, $ROCH_2Cl$, and $C_6H_5N_2Cl$

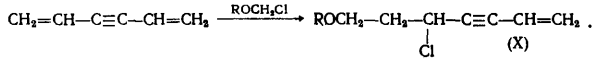
Petrov and coworkers [112] showed that electrophilic addition of methyl hypobromite to divinylacetylene, isopropenylvinylacetylene, and 3-methylhepta-2,6-dien-4-yne takes place at the double bond, and in the case of the last two dienynes only in the substituted vinyl group. Thus in this

case electrophilic addition of methyl hypobromite occurs in accordance with the electronic configuration of these dienes:

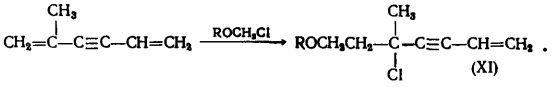


Ethyl hypochlorite[113] adds to DVA in a similar manner to methyl hypobromite[112].

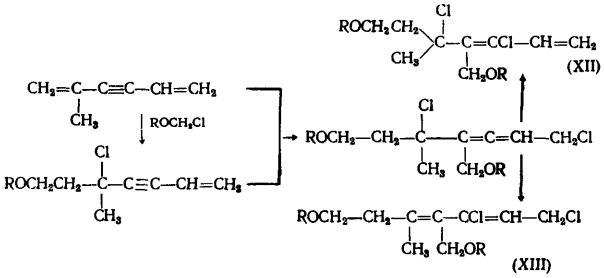
In the presence of zinc chloride in ethereal solution α-chloroalkyl ethers add on to DVA[114,115] at the 1,2-position with the formation of vinylacetylene chlorides (X):



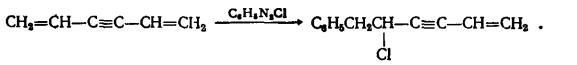
It has been established that in the case of isopropenylvinylacetylene the chloroalkyl ether adds to the double bond with the higher electron density and the monochloride (XI) is formed:



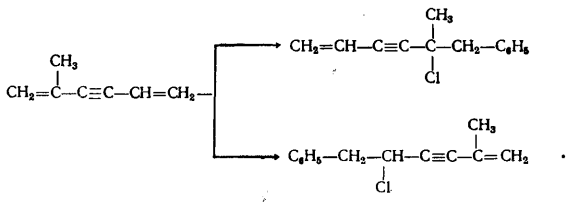
With isobutenylvinylacetylene and Δ^1-cyclohexenylvinylacetylene the reaction proceeds similarly. Apparently the addition of the second molecule of α-chloroalkyl ether to the vinylethynyl radical of the newly formed monochloride takes place at the 1- and 4-positions, yielding an allene dichloride, which under the conditions of the experiment isomerises into two dichlorides (XII) and (XIII). It has been established that the dichloride (XII) can isomerise to the dichloride (XIII) both under the conditions of the reaction and on standing without a catalyst. The reverse isomerisation is not observed. These dichlorides are obtained both when one molecule of α-chloroalkyl ether reacts with the monochloride (XI) and by direct interaction of two molecules of the α-chloroalkyl ether with isopropenylvinylacetylene:



On chloroarylation divinylacetylene combines with the aryl group and chlorine, which add mainly to the vinyl group:

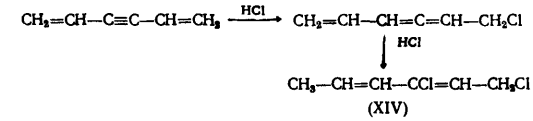


In the case of isopropenylvinylacetylene reaction takes place both in the vinyl and the isopropenyl groups with the formation of a mixture of the corresponding chlorides, but in each case the phenyl group adds on only to the terminal carbon atom of the double bond[116]:

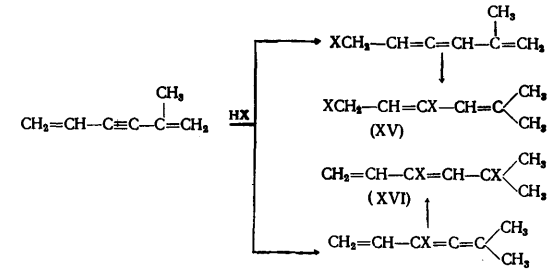


11. ADDITION OF HYDROGEN HALIDES

In the presence of cuprous chloride and ammonium chloride in aqueous solution hydrogen chloride adds on to DVA at the 1- and 4-positions, this being followed by the addition of a second molecule of hydrogen chloride at the other end of the molecule, also at the 1- and 4-positions, so that the final product is 1,3-dichlorohexa-2,4-diene (XIV):[117,118]

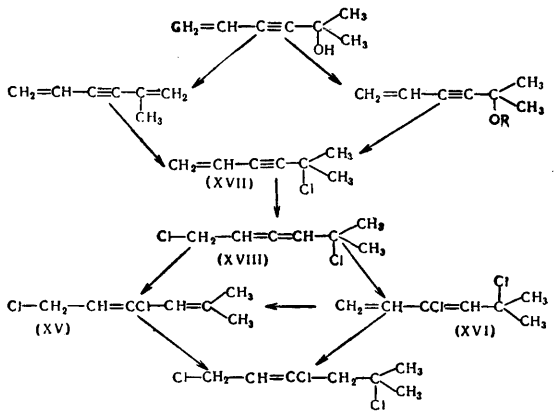


Hydrogen chloride undergoes successive addition to vinylisopropenylacetylene at the 1- and 4-positions, yielding a mixture of 1,3-diene dichlorides (XV) and (XVI).[119,120] Similar results were obtained in the hydrochlorination of dimethylvinylethynylmethanol and chlorodimethylvinylethynylmethane[121]. However, the dichlorides were not isolated in the pure state. The addition of hydrogen bromide takes place similarly[122]:

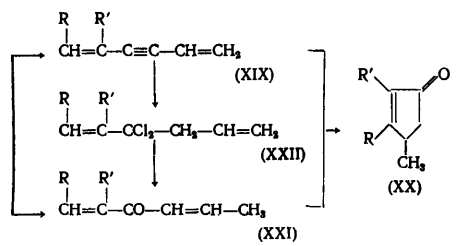


As a result of the further investigation of the hydrochlorination of these compounds, Nazarov and coworkers concluded that only the primary dichloride (XV) is formed[123]. However, subsequent detailed study of the hydrochlorination of isopropenylvinylacetylene, dimethylvinylethynylmethanol, and chlorodimethylvinylethynylmethane established that Nazarov's initial hypothesis was correct and that hydrochlorination indeed results in the formation of two isomeric dichlorides (XV) and (XVI).[124] But in all cases the addition of the first molecule of hydrogen chloride involves the formation of the monochloride (XVII) in the first stage, *i.e.* the first molecule of hydrogen chloride adds on at the 1- and 2-positions of the substituted vinyl group of isopropenylvinylacetylene. The monochloride (XVII) is also formed when hydrogen chloride reacts with dimethylvinylethynylmethanol or its methyl ether, the hydroxy- or the methoxy-group being replaced by chlorine. Thus the above findings show that in both cases the monochloride (XVII) forms in the first stage of the reaction. It appears that subsequently hydrogen chloride adds on to the vinylethynyl group of the monochloride at the 1- and 4-positions, with the formation of the intermediate allene chloride (XVIII), which under the conditions of the experiment isomerises to the dichlorides (XV) and (XVI). It was shown that under the given experimental conditions the dichloride (XVI) isomerises to the dichloride (XV), but the reverse isomerisation has not been observed. Hence it can be supposed that the dichloride (XVI) can be obtained both by the isomerisation of the dichloride (XVIII) and by the addition of a second molecule of hydrogen chloride to chlorodimethylvinylethynylmethane at the 3- and 4-positions. The dichloride (XV) can form as a result of the isomerisation of either one of the dichlorides (XVI) and (XVIII).

It has been shown that in the presence of the cuprous chloride and ammonium chloride catalysts the dichloride (XV) predominates in the mixture of (XV) and (XVI), whereas in the presence of aluminium chloride the main product is (XVI). Both dichlorides undergo hydrochlorination at 60° with the formation of the same trichloride:



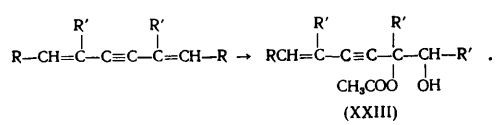
Nazarov and Yanbikov[125] established that disubstituted divinylacetylenes (XIX) undergo cyclohydration under the action of concentrated hydrochloric acid at 60–70° with the formation of the corresponding cyclopentenones (XX), and they were unable to isolate any products of the addition of hydrogen chloride to dienynes. They concluded that either direct hydration of the triple bond of these compounds takes place with the formation of the corresponding divinylketone (XXI), which under the conditions of the experiment cyclises into the cyclopentenone, or the divinylketone forms as a result of the addition of two molecules of hydrogen chloride to the triple bond of the dienyne followed by hydrolysis of the resulting dichloride (XXII):



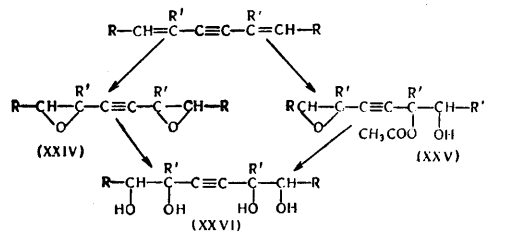
It is interesting to note that hydrochlorination of alkyl-β-methoxyethylvinylethynylmethanol and the product of its dehydration, alkoxydienyne, yields isomeric dichlorides, while the expected cyclopentenones are not formed[126].

12. OXIDATION OF DIVINYLACETYLENE HYDROCARBONS

Malenok and coworkers studied the oxidation of divinylacetylene hydrocarbons with acetyl hydroperoxide[127–129]. They showed that, when the oxidising agent reacts with the dienyne hydrocarbons in stoichiometric proportions, the vinylacetylene alcohol-acetate (XXIII) is formed:

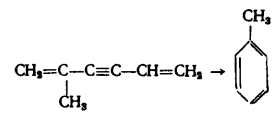


When two molecules of acetyl hydroperoxide are used per molecule of dienyne, the main products are the corresponding acetylene dioxides (XXXIV), together with a small amount of the monoxide (XXV). The latter is a product of the reaction between the newly formed dioxide and acetic acid. Acetylenic tetrols (XXVI) were obtained by the hydrolysis of the oxides (XXIV) and (XXV):

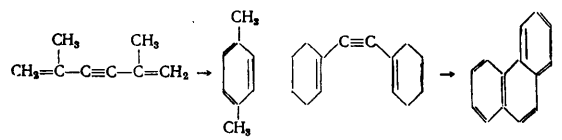


13. CYCLISATION

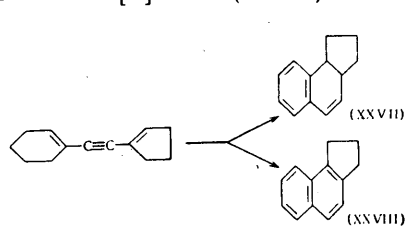
The aromatisation of divinylacetylene hydrocarbons and their partially hydrogenated derivatives has been studied in detail by Kotlyarevskii and coworkers[130–136]. Some data on this problem also exist in the patent literature[137–139]. The aromatisation of divinylacetylene hydrocarbons is of interest from the point of view of synthesis, because it makes possible the controlled synthesis of aromatic hydrocarbons with a prescribed structure which depends on that of the initial dienynes. Kotlyarevskii and Zanina[131] showed that, when isopropenylvinylacetylene (or products of its partial hydrogenation, up to the absorption of three molecules of hydrogen) is passed over the catalyst $MgO–CrO_3–Al_2O_3$ (2 : 18 : 80) at high temperatures, toluene is obtained in good yield:



Benzene was prepared similarly from DVA in 15–20% yields. Under these conditions diisopropenylacetylene cyclises into *p*-xylene[133], while di-Δ^1-cyclohexenylacetylene yields phenanthrene in 70% yield[134]:

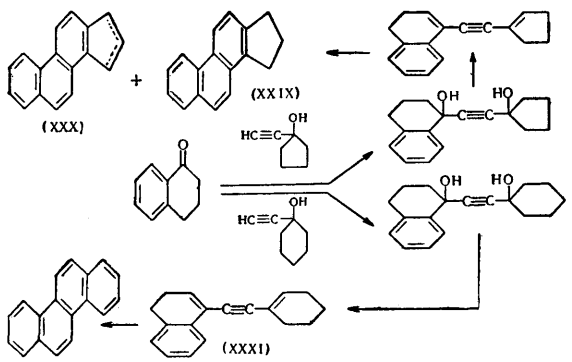


The method has also been used for the synthesis of tri- and tetra-cyclic condensed aromatic hydrocarbons, from which condensed hydrocarbons with a five-membered ring can be obtained by catalytic dehydrocyclisation. When Δ^1-cyclohexenyl-Δ^1-cyclopentenylacetylene is passed over a magnesium oxide-promoted aluminium oxide–chromium oxide catalyst, dehydrocyclisation takes place with the formation of 2,3,10,11-tetrahydro-1*H*-benz[*e*]indene (XXVII) and 2,3-dihydro-1*H*-benz[*e*]indene (XXVIII):



These compounds are of considerable interest for the preparation of polycyclic compounds with interesting carbon skeletons.

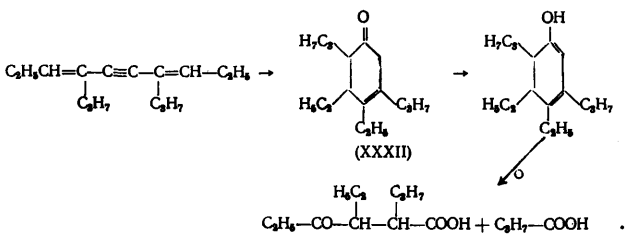
15,16-Dihydro-17*H*-cyclopenta[*a*]phenanthrene (XXIX) and 17*H*-cyclopenta[*a*]phenanthrene (XXX) were synthesised from α-tetralone and 1-ethynylcyclopentan-1-ol as follows[136]:



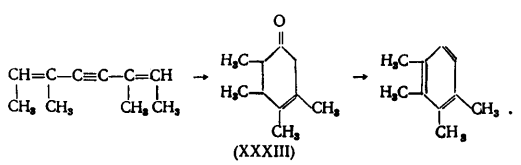
By a similar procedure chrysene was obtained from α-tetralone and 1-ethynylcyclohexan-1-ol *via* the dienyne (XXXI).

14. CYCLOHYDRATION

By the action of sulphuric acid on 4,7-dipropyldeca-3,7--dien-5-yne in acetic acid solution, Blomquist and Marvel[48] obtained 2,5-dipropyl-3,4-diethylcyclohexenone (XXXII) whose structure was proved by ozonolysis. The authors assumed that before ozonolysis the ketone (XXXII) undergoes enolisation as a result of which β-ethyl-γ-oxo-α--propylhexanoic and propionic acids are formed:

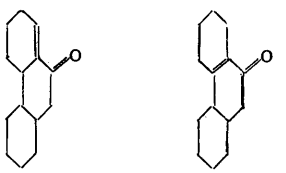


Later Mitchell and Marvel[50] established that diisopropenylacetylene cannot undergo the above cyclisation, but 3,6-dimethylocta-2,6-dien-4-yne does so with the formation of the cyclic ketone (XXXIII). The structure of the latter was demonstrated by Clemmensen reduction, followed by dehydrogenation to 1,2,3,4-tetramethylbenzene:

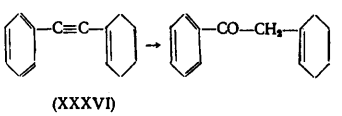


Marvel and coworkers[49] subjected di-Δ¹-cyclohexenylacetylene to cyclohydration under the action of formic acid and isolated two cyclic ketones — liquid and crystalline. The structure of the liquid isomer, dodecahydro-9-phenanthrone, was demonstrated by hydrogenation to perhydrophenanthrene; the authors were unable to establish the structure of the crystalline isomer.

Linstead and coworkers[140] also state that cyclisation of di-Δ¹-cyclohexenylacetylene results in the formation of two isomeric ketones. However, unlike Marvel, they found that both ketones are crystalline (m.p. 39° and 88°). Spectroscopic analysis showed that they are αβ-unsaturated ketones, in agreement with the results of other workers[141,142]. It was shown that dehydrogenation in the presence of platinum yields phenanthrene while the hydrogenation of each isomer separately results in the formation of the same 9-oxotetrahydrophenanthrene. On the basis of these findings, the authors attributed the structure (XXXIV) to the low-melting isomer and the structure (XXXV) to the high-melting isomer.

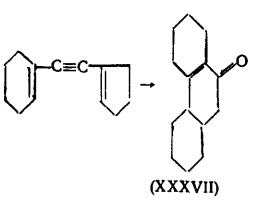


It has been established that when one of the double bonds of the dienyne is present in a six-membered ring, as in compound (XXXVI), the dienyne is still hydrated to the corresponding unsaturated ketone, but the latter can no longer undergo cyclisation into the expected cyclic ketone[56,59]:

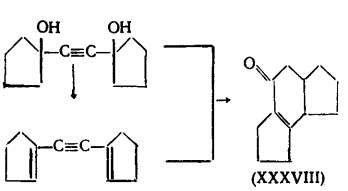


It has also been shown that dienynes with at least one hydrogen atom at the terminal carbon atom undergo cyclisation.

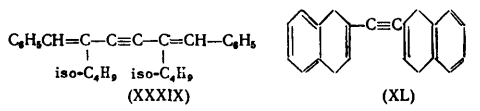
Under the action of formic acid Δ¹-cyclohexenyl-Δ¹--cyclopentenylacetylene cyclises into the tricyclic ketone (XXVII):[143]



When zinc amalgam and hydrochloric acid act upon di-Δ¹--cyclopentenylacetylene and the corresponding acetylene glycol, the latter compounds cyclise into the corresponding cyclohexane derivatives (XXXVIII):[56]

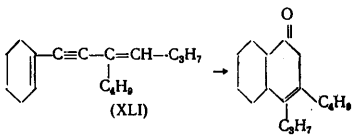


It is interesting that, when both double bonds of the diene are conjugated with an aromatic ring [compounds (XXXIX) and (XL)], cyclohydration does not occur.

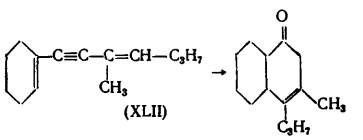


(XXXIX) (XL)

It has been established that the dienynes (XLI) and (XLII) are also capable of cyclising under the action of formic acid[54]:

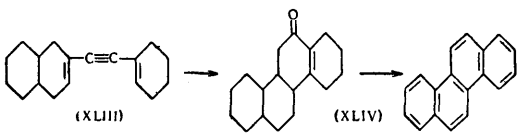


(XLI)



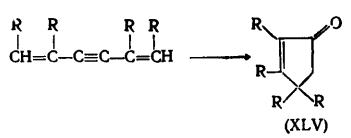
(XLII)

Cyclohydration of the dienyne (XLIII) yields the tetracyclic ketone (XLIV). The latter was subjected to Clemmensen reduction and dehydrogenated with platinum, the final product being chrysene[144]:



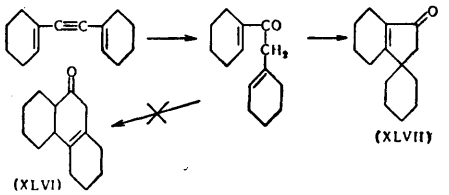
(XLIII) (XLIV)

The investigations of Marvel and coworkers, who studied the cyclohydration of a number of substituted dienynes quoted above, undoubtedly yielded erroneous results. This follows from the work of Nazarov and coworkers[1] on numerous and various examples. The latter showed that cyclohydration of dienynes and the cyclisation of divinyl ketones results in the exclusive formation of substituted cyclopentenones† and not cyclohexenones as stated by Marvel and coworkers. In particular, on the example of 3,6-dimethylocta-2,6-dien-4-yne Nazarov and Verkholetova[145] showed that not only asymmetric dienynes but also symmetric tetrasubstituted dienynes undergo cyclisation into the corresponding cyclopentenones (XLV) under these conditions:



(XLV)

Independently of one another, Nazarov and coworkers[146,147], Bogert and coworkers[148], and Linstead and Doering[149] showed that di-Δ^1-cyclohexylacetylene also readily undergoes cyclohydration under the above conditions with the formation not of the so-called "Marvel's ketone" *i.e.* a ketone with a phenanthrene skeleton (XLVI) but a ketone with a spiran structure (XLVII):



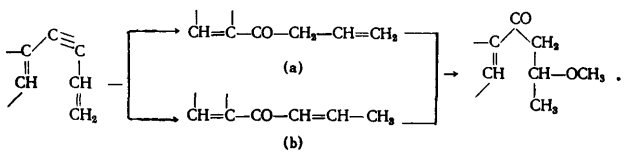
(XLVI) (XLVII)

The final proof that this ketone is not a phenanthrene derivative is provided by the detailed investigations of Linstead and coworkers[149].

15. SYNTHESIS OF β-ALKOXYKETONES BY HYDRATION OF DIVINYLACETYLENE HYDROCARBONS IN AQUEOUS SOLUTIONS OF ALCOHOLS

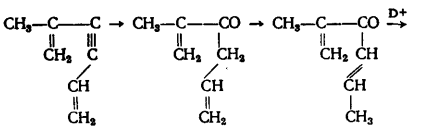
In contrast to acetylene derivatives, until recently the hydration of divinylacetylene hydrocarbons was not investigated at all. Nazarov and coworkers were the first to develop a very simple and effective method of hydrating divinylacetylene hydrocarbons[1]. The latter, on heating in aqueous solutions of methanol in the presence of small amounts of sulphuric acid and mercuric sulphate, are smoothly hydrated to the corresponding dienones, which under the conditions of the experiment combine with one molecule of methanol with the formation of β-methoxyketones, in most cases in high yields.

In all cases the addition of water takes place in such a way that the oxygen is directed to the acetylene carbon atom which is combined with the substituted vinyl radical:

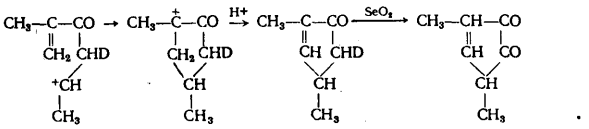


(a) (b)

In order to establish the structure of the dienones, (a) and (b), Nazarov and coworkers[151] prepared deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one by the action of deuterated phosphoric acid on the dienone obtained on hydration of 2-methylhexa-1,5-dien-3-yne. By oxidation with selenium dioxide, they convincingly showed that the resulting 2,4-dimethyl-Δ^2-cyclopentene-1,5-dione does not contain deuterium. It follows therefore that deuterium was present in deutero-2,4-dimethyl-Δ^2-cyclopenten-1-one at carbon atom 5, *i.e.* in the methylene group adjacent to the carbonyl. This constitutes proof that 2-methylhexa-1,4-dien-3-one (B) cyclises and not the isomeric 2-methylhexa-1,5-dien-3-one (A).

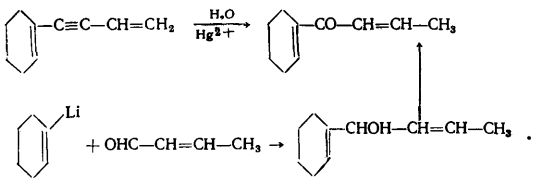


(A) (B)



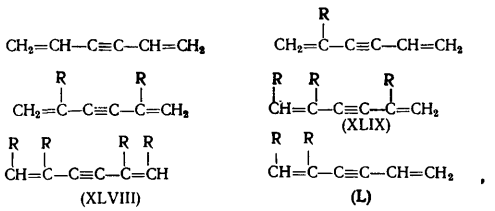
† Nazarov's review[1] deals with this problem. We may note that at present even in the non-Soviet literature this reaction is known as the Nazarov[150] and not Marvel cyclisation.

Quite recently Nazarov and Zaretskaya[152] demonstrated experimentally that hydration of Δ^1-cyclohexenylvinylacetylene yields not allyl Δ^1-cyclohexenyl ketone but Δ^1-cyclohexenylpropenyl ketone. The latter was also synthesised in a different way and proved to be identical with the product obtained on hydration of Δ^1-cyclohexenylvinylacetylene:



Thus the work of Nazarov shows that hydration of divinylacetylene hydrocarbons results in the formation not of allyl vinyl ketones but of the isomeric divinyl ketones.

According to the ease of hydration, Nazarov[1] divides dienyne into three groups:



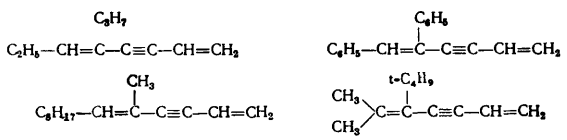
where R = alkyl, aryl, or a cyclic residue.

Group (XLVIII): symmetrical dienynes, in particular divinylacetylene itself; the compounds are hydrated at the lowest rate (in the course of 15–20 h) with good yields of β-methoxy-ketones.

Group (L): asymmetric disubstituted dienynes; they are hydrated very readily, usually in 1–2 h, with the formation mainly of β-methoxy-ketones in quantitative yields.

Group (XLIX): asymmetric mono- and tri-substituted dienynes; as regards ease of hydration they occupy an intermediate position.

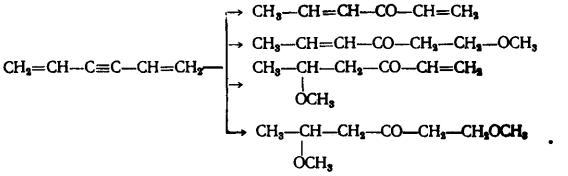
Thus the rate of hydration of dienynes to a great extent depends on the disposition of the substituents in them, an asymmetric disposition favouring hydration, which is undoubtedly associated with the increased polarity of the molecule. It has been shown that the dipole moments of asymmetric dienynes are higher[153]. This explains the fact that hydration of asymmetric dienynes occurs in only one way, the elements of water adding to the triple bond in such a way that the oxygen always becomes attached to the carbon atom which is linked to the substituted vinyl group. It has also been established that not only the disposition but the nature of the substituents has a very great effect. Introduction into the dienyne molecule of aromatic and large aliphatic residues slows down the reaction, which is probably due to steric hindrance. Thus, for example, the following dienynes are difficult to hydrate despite their asymmetric structure[154-157]:



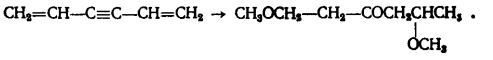
Thus divinylacetylene itself and symmetrically substituted dienynes are the most difficult to hydrate. Introduction of one and particularly two substituents into one of the vinyl radicals of the dienyne (asymmetric substitution) greatly accelerates the reaction. As the size of the substituent increases, the rate of hydration again falls.

Attempts to hydrate divinylacetylene to allyl vinyl ketone under the conditions of Kucherov's reaction have been unsuccessful[77]. Only a very small quantity of a product was isolated, to which the structure of the allyl vinyl ketone was attributed without proof. As shown later by Nazarov and Zaretskaya[104,157], the physical constants of this substance are similar to those of the products of the further hydration of allyl vinyl ketone, namely 2-methyltetrahydro-4-pyrone.

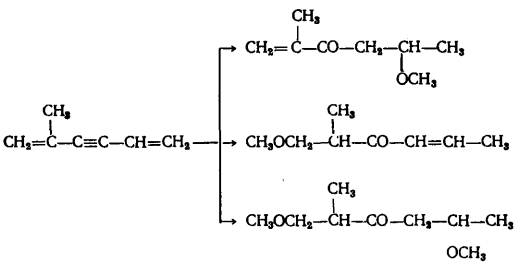
The hydration of divinylacetylene was achieved for the first time[158] in 1942 in aqueous methanol in the presence of sulphuric acid and mercuric sulphate. The resulting dienone (propenyl vinyl ketone) was converted under the conditions of the experiment into a mixture of 1,5-dimethoxyhexan-3-one and unsaturated methoxy-ketones by the addition of one or two molecules of methanol:



This reaction was studied in detail, the concentration of methanol, the reaction time, the temperature, and the composition of the catalyst being varied. As a result, it was found[159] that addition of sulphuric acid is not only unnecessary but that it actually enhances resinification. In the presence of mercuric sulphate without sulphuric acid in 90–95% aqueous alcohol divinylacetylene is hydrated in the course of 20 h, a good yield of 1,5-dimethoxyhexan-3-one being obtained:

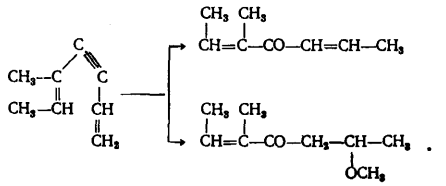


Isopropenylvinylacetylene, which is obtained in good yield on dehydration of dimethylvinylethynylmethanol, is relatively readily hydrated under similar conditions[104,105]. The hydration of this dienyne in aqueous methanol yields isopropenyl propenyl ketone, which under the conditions of the experiment combines with one or two molecules of the alcohol with the formation of the corresponding β-methoxy--ketones:

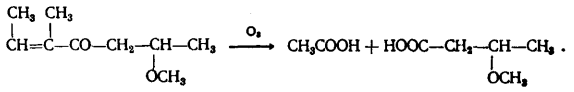


Like the above dienynes, 5-methylhepta-1,5-dien-3-yne very readily undergoes total hydration in aqueous solutions of methanol at 60–65° in the presence of small amounts

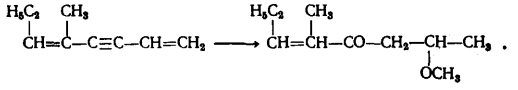
of sulphuric acid and mercuric sulphate, the products being the methoxy-ketone and a mixture of two isomeric dienones[37] which differ sharply from each other in their physical constants. When methanol is split off from the methoxy-ketone, only the high-boiling isomer of the dienone is formed. On hydrogenation both isomers yield only one saturated ketone:



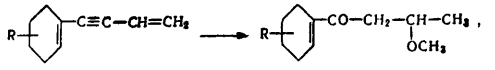
On more prolonged heating of the dienyne under the above conditions, the main product is 2-methoxy-5-methylhex-5-en-4-one. On ozonolysis of the methoxy-ketone, acetic and β-methoxybutyric acids are formed in good yields:



In another investigation Nazarov and Zaretskaya[160] studied the hydration of 5-methylocta-1,5-dien-3-yne, obtained by dehydration of methylpropylvinylethynylmethanol. As in the previous case, the dienyne hydrates readily with the formation of 5-methylocta-2,5-dien-4-one, which like the previously investigated 5-methylhepta-2,5-dien-5-one, is apparently obtained as a mixture of two geometrical isomers. In the presence of mercuric sulphate methanol readily adds to the propenyl radical of each isomer, the corresponding methoxy-ketones being formed:

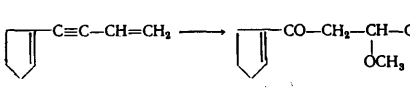


In the hydration of alicyclic dienynes, as in the hydration of other asymmetrically substituted divinylacetylene hydrocarbons, the addition of water to the triple bond is such that the oxygen always combines with the carbon atom linked to the substituted vinyl radical. Addition of water which would result in the formation of tetrahydrobenzyl vinyl ketone is not observed[161].

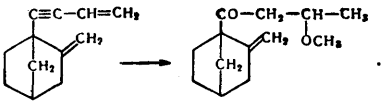


where R = H, CH_3.

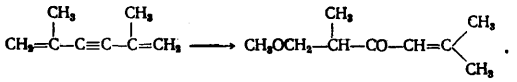
Under the above conditions the hydration terminates after 2 h. On further heating of the reaction mixture for 5–6 h almost the entire dienone is converted into Δ^1-cyclohexenyl β-methoxypropyl ketone. Ozonolysis of the latter gives β-methoxypropionic and adipic acids. On heating in 80–85% methanol under the above conditions Δ^1-cyclopentenylvinylacetylene is readily hydrated with the formation of two isomeric dienones (liquid and crystalline) which under the conditions of the experiment readily combine with methanol yielding the same Δ^1-cyclopentenyl β-methoxypropyl ketone. The latter on distillation with *p*-toluenesulphonic acid splits off methanol, yielding only the crystalline Δ^1-cyclopentenyl propenyl ketone[162].



The corresponding β-methoxy-ketone is also formed[163] on hydration of vinylethynylcamphene (obtained on dehydration of vinylethynylborneol):

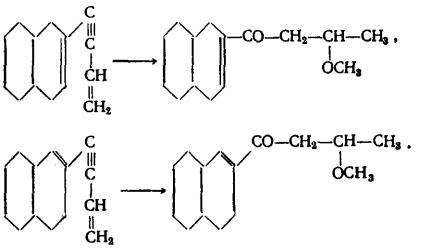


On heating in 90% methanol in the presence of sulphuric acid and mercuric sulphate, 2,5-dimethylhexa-1,5-dien-3-yne (obtained by dehydration of tetramethylbutynediol) is hydrated to 2,5-dimethylhexa-1,5-diene-3-one[164]. The hydration of this symmetrically substituted dienyne takes place with much greater difficulty than that of asymmetric dienynes.



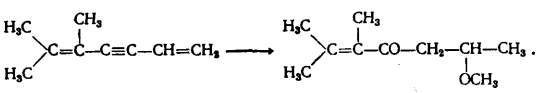
Under the conditions of the hydration reaction, methanol adds to the isopropenyl group of 2,5-dimethylhexa-2,5-dien-3-one with the formation of 2,5-dimethyl-1-methoxyhex-4-en-3-one. The latter on distillation in the presence of *p*-toluenesulphonic acid splits off methanol with the reformation of the initial dienone. Hydration of 3,6-dimethylocta-2,6-diene-4-yne yields 3,6-dimethylocta-2,5-dien-4-one which is incapable of combining with methanol[145].

When 2-vinylethynyl-2-decanol is heated with 50% sulphuric acid for 5 h at 55–60°, it is dehydrated yielding a mixture of 2-vinylethynyl-$\Delta^{1(2)}$-octalin and 2-vinylethynyl-$\Delta^{2(3)}$-octalin. When this mixture is hydrated in 95° methanol in the presence of sulphuric acid and mercuric sulphate, the product (70% yield) is a mixture of liquid and crystalline propenyl $\Delta^{1(2)}$-octahydro-2-naphthyl ketones[165,166], which can be readily separated by freezing out. On more prolonged hydration of the dienynes (more than 5 h), the principal, or even the only products, are methoxy-ketones which on vacuum distillation in the presence of *p*-toluenesulphonic acid split off methanol, and the initial dienones are reformed; hydrogenation yields the corresponding saturated methoxy-ketone:

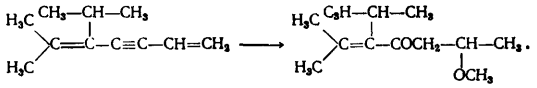


The structure of the unsaturated methoxy-ketones has been demonstrated by ozonolysis.

On heating in aqueous methanol under the above conditions, 5,6-dimethylhepta-1,5-dien-3-yne is quantitatively hydrated with the formation of 5,6-dimethylhepta-2,5-dien-4-one, which under the conditions of the experiment combines with one molecule of methanol and is converted into 5,6-dimethyl-2-methoxyhept-5-en-4-one[167]. On vacuum distillation in the presence of *p*-toluenesulphonic acid, the latter splits off methanol and reforms the initial dienone:

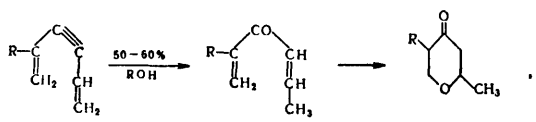


5-Isopropyl-6-methylhepta-1,5-dien-3-yne, obtained by dehydration of diisopropylvinylethynylmethanol on heating in aqueous methanol in the presence of sulphuric acid and mercuric sulphate, is readily hydrated to the corresponding dienone, whose propenyl group combines with methanol and 2-methoxy-5-isopropyl-6-methylhept-5-en--4-one is formed[168]. On careful heating of the latter in the presence of 0.5% of *p*-toluenesulphonic acid (15 min at 120–130°), methanol is split off with the reformation of the initial dienone (in high yield), which on more prolonged heating cyclises into the corresponding pentenone:



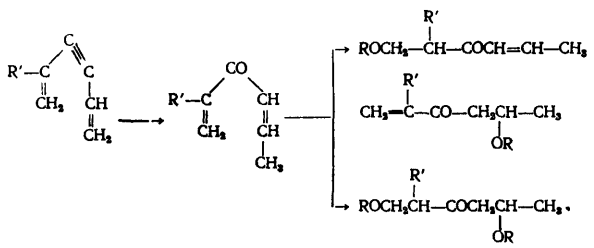
The above findings show that hydration of divinylacetylene hydrocarbons in aqueous methanol may be regarded as the simplest and most convenient method of the synthesis of β-methoxy-ketones. It has been established[169] that dienones can be hydrated in different alcohols, which makes it possible to obtain a wide variety of β-alkoxy-ketones. Depending on the conditions, this reaction results in the formation of β-alkoxy-ketones or tetrahydro-γ-pyrones. In order to obtain β-alkoxy-ketones, water is gradually added to the heated mixture of the alcohol and the dienyne, while tetrahydro-γ-pyrones are obtained when the dienyne is added dropwise to the water–alcohol mixture. The ease and the time required for the hydration of dienynes depend also on the nature of the alcohol used, the rate of hydration being lower when the latter has a branched structure and a high molecular weight.

When divinylacetylene and isopropenylvinylacetylene are heated in 50–60% aqueous ethanol or methanol in the presence of mercuric sulphate and sulphuric acid, the corresponding tetrahydro-γ-pyrones are obtained in 50% yield:

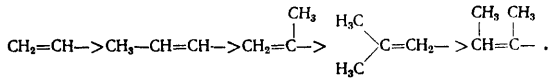


where R = H, CH_3.

In the hydration of divinylacetylene in 80–95% alcohol, considerable amounts of a mixture of alkoxy-ketones, whose structure has been elucidated by ozonolysis, are formed in addition to the pyrone:



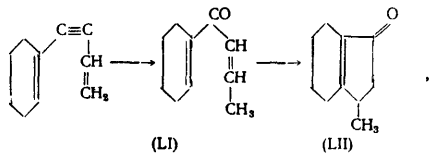
It has been shown that a disubstituted vinyl group is incapable of combining with alcohols (even methanol), the propenyl group combines with alcohols more readily than the isopropenyl group, and that the unsubstituted vinyl group undergoes the addition reaction most readily[170]. With respect to the rate of addition of the alcohols (and also amines and other compounds) to αβ-unsaturated ketones, vinyl radicals can be arranged in the following series[169]:



It must be noted that, when the hydration of dienynes is carried out in solution in isopropenyl alcohol, the only reaction product is the monoalkoxy-ketone (R = iso-C_3H_7), *i.e.* isopropenyl alcohol proves to be quite incapable of adding to the isopropenyl group of isopropenyl propenyl ketone.

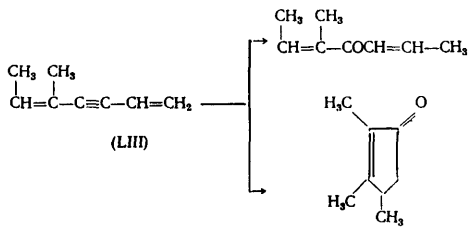
Disubstituted asymmetric enyne hydrocarbons are also readily hydrated in aqueous alcoholic solutions in the presence of mercuric sulphate and sulphuric acid. The hydration is completed in 3–4 h but here instead of the expected β-alkoxy-ketones the hydration products are only the corresponding unsaturated ketones. Prolonged experiments (24 h) have shown that, instead of combining with the alcohols, these unsaturated ketones cyclise into the corresponding cyclopentenones.

On heating in 95–98% ethanol or butanol for 3–5 h in the presence of mercuric sulphate, Δ^1-cyclohexenylvinylacetylene is completely hydrated to the corresponding unsaturated ketone (LI) [169] which in more prolonged experiments partly cyclises into 1-methyl-4,5,6,7-tetrahydroinden-3-one (LII):



(LI) (LII)

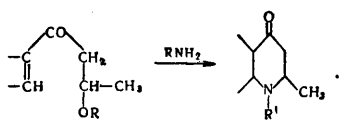
hydration of 3-methylhepta-2,6-dien-4-yne (LIII) in ethanol or butanol for 20–26 h yields a mixture of 3-methylhepta--2,5-dien-4-one and 2,3,4-trimethylcyclopent-2-en-1-one:



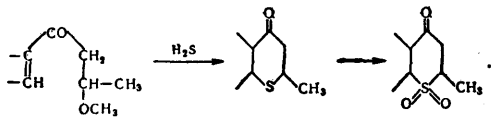
(LIII)

The above data show that, under the above conditions of the hydration reaction, ethanol and butanol are incapable of adding to the αβ-unsaturated ketones described. This makes it possible to hydrate asymmetric disubstituted enyne hydrocarbons to the corresponding αβ-unsaturated ketones, which could not be achieved when these dienynes were hydrated in methanol, since under the conditions of the hydration reaction the unsaturated ketones formed are capable of combining with one molecule of methanol to yield β-methoxy-ketones. The divinyl ketones thus obtained have become readily available and are now the simplest unsubstituted starting materials for the synthesis of a wide variety of carbocyclic and heterocyclic ketones of the tetrahydropyran, thiopyran, and piperidine series. For example, when aqueous ammonia or aqueous solutions of primary amines are allowed to act upon β-alkoxy-ketones,

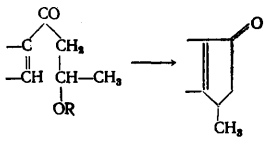
the corresponding γ-piperidones are obtained in high yields[171]:



The action of hydrogen sulphide on allyl vinyl ketones in alcoholic solutions of sodium acetate or amines results in the formation, in high yields, of a wide variety of tetrahydro-γ-thiopyrones[172] which are readily oxidised by potassium permanganate in acetone solution to the corresponding sulphones:



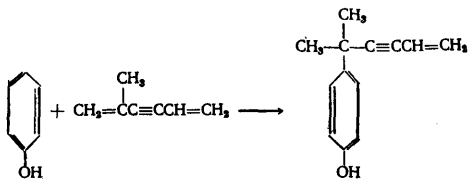
When treated with phosphoric acid (and also other acids), allyl vinyl ketones are extremely readily and often quantitatively cyclised into the corresponding cyclopentenones[1]:



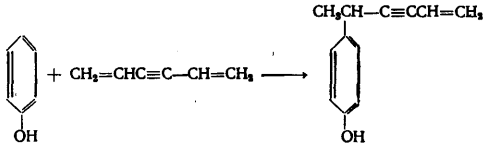
The discovery of very simple methods for the preparation of heterocyclic ketones (γ-piperidones and tetrahydrothiopyrones), which were previously difficult to obtain, has led to the recent extensive development of the search for and synthesis of new physiologically active and medicinal substances. In particular, it has been possible to synthesise a whole series of new ethers of the piperidine series with exceptionally high analgesic activity, several times greater than that of morphine and other natural products.

16. ALKYLATION AND CYCLOALKYLATION

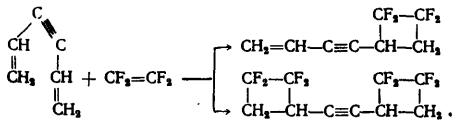
It has been shown that, when isopropenylvinylacetylene is heated with phenol in the presence of phosphoric acid, p-substituted phenols are obtained[173,174]:



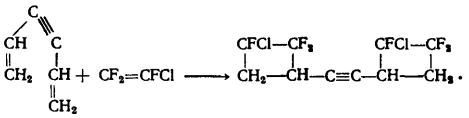
The alkylation of phenol with DVA takes place similarly[175]:



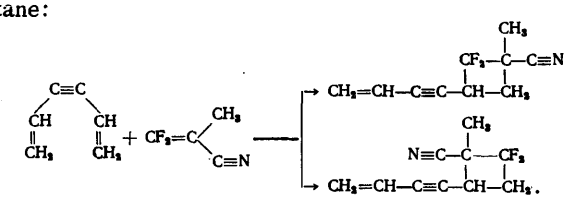
Quite recently it has been shown[176] that heating of DVA with tetrafluoroethylene in the presence of 0.1 g of N-phenyl-β-naphthylamine for 11 h at 125° results in the formation of bis-(2,2,3,3-tetrafluorocyclobutyl)acetylene and 1,1,2,2-tetrafluoro-3-vinylethynylcyclobutane. The products of addition to the triple bond were not obtained.



Chlorotrifluoroethylene condenses with DVA in 6.5 h at 150° with the formation of bis-(2-chloro-2,3,3-trifluorocyclobutyl)acetylene:

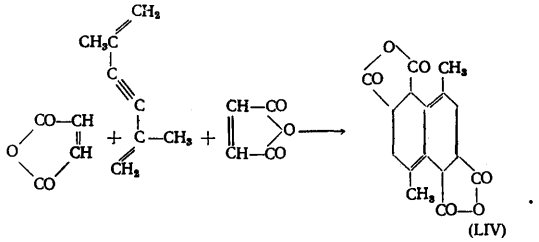


Condensation of DVA with $\beta\beta$-difluoro-α-methacrylonitrile yields an adduct consisting of a mixture of the isomers of 1-vinylethynyl-2,2-difluoro-3-methyl-3-cyanocyclobutane and 1-vinylethynyl-3,3-difluoro-2-methyl-2-cyanocyclobutane:



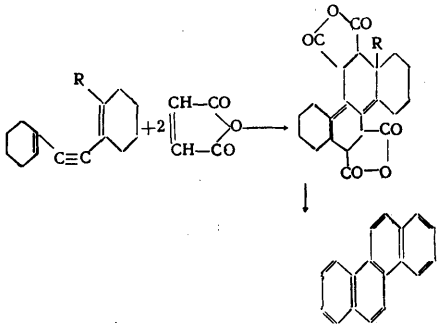
17. DIENE SYNTHESIS

Marvel and coworkers[48] were the first to establish that diisopropenylacetylene is capable of undergoing diene synthesis with maleic anhydride when a mixture of the two compounds in xylene solution is heated in the presence of aqueous alkali. However, these workers isolated an amorphous compound whose structure was not determined. Later, this reaction was studied in greater detail by other investigators[177], who showed that bicyclic compounds with methyl substituents (LIV) are indeed formed:



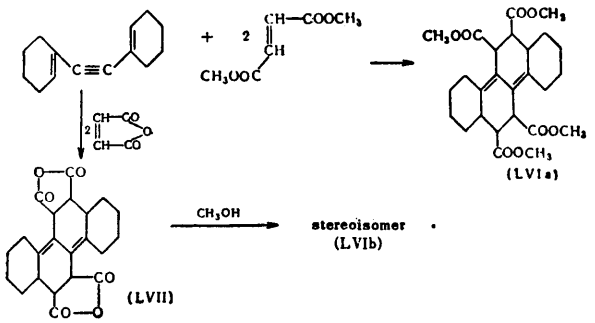
(LIV)

Subsequently this method was used for the synthesis of compounds of the hydrochrysene series with angular methyl groups. It was shown that condensation of di-Δ^1-cyclohexylacetylene (or its 2-methyl derivative) with two molecules of maleic anhydride yields the tetracyclic adduct (LV), whose decarboxylation and dehydrogenation give chrysene[178]:

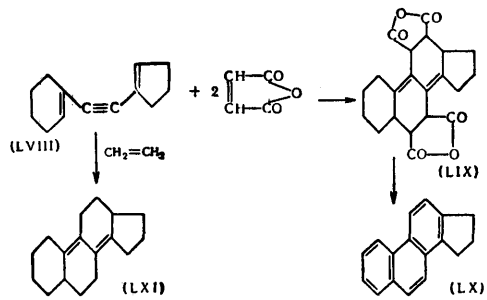


(LV)

where R = H, CH_3. Dicyclohexylideneacetylene undergoes diene synthesis with maleic anhydride[179] and dimethyl fumarate[180]. The resulting ester (LVIa) proves to be the stereoisomer of the ester (LVIb), which was obtained by the reaction of methanol with the adduct (LVII):

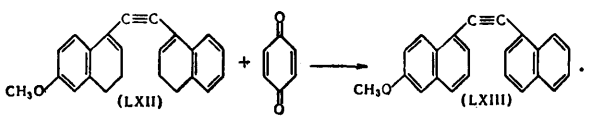


The addition of dienophiles to dienynes was studied in detail by Butz and coworkers[181,182]. Δ^1-Cyclohexenyl-Δ^1--cyclopentenylacetylene (LVIII) also undergoes diene synthesis with the formation of the adduct (LIX) whose structure was demonstrated by dehydrogenation, using palladium on carbon, to 15,16-dihydro-17*H*-cyclopenta[*a*]phenanthrene‡ (LX):[181,182]



Condensation of the dienyne (LVIII) with ethylene yields the tetracyclic compounds (LXI).

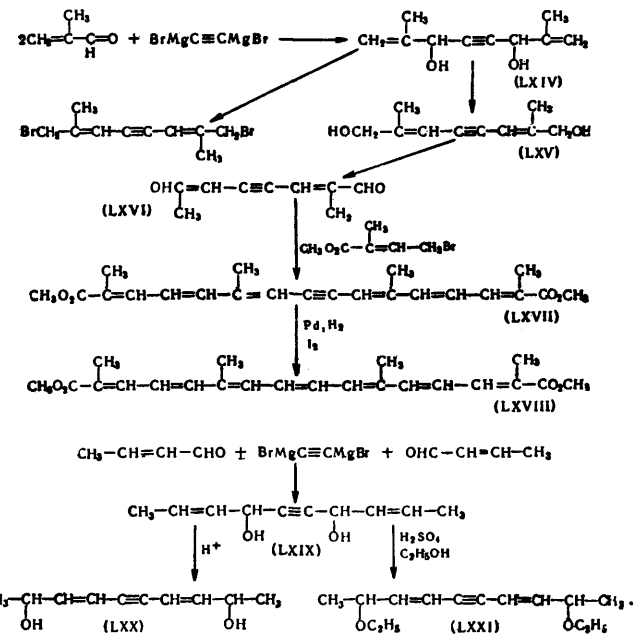
It is interesting to note that, when an attempt is made to condense the dienyne (LXII) with *p*-benzoquinone[183], instead of the expected reaction dehydrogenation of the dienyne with the formation of the aromatic compound (LXIII) occurs:



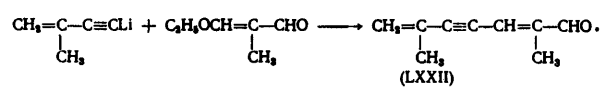
18. ALDEHYDES AND GLYCOLS OF THE DIVINYLACETYLENE SERIES

Aldehydes of the divinylacetylene series have been prepared for the synthesis of carotenoid compounds[184-187]. The synthesis was achieved as follows. Reaction of α-methylacrolein with acetylene di(magnesium bromide) gave the corresponding diol (LXIV) which was subjected to anionotropic isomerisation to give the divinylacetylene glycol (LXV) in good yield. Oxidation of the latter with manganese dioxide gave the divinylacetylene aldehyde (LXVI), whose condensation with methyl α-methyl-β-bromoethylacrylate followed by selective hydrogenation of the resulting dehydrocrocetin (LXVII) gave a good yield of the dimethyl ester of 8,8-*cis*--crocetin (LXVIII).

By reaction of crotonaldehyde with the acetylene di(magnesium bromide) derivative, Heilbron and coworkers[186] obtained the corresponding acetylene glycol (LXIX). The latter was subjected to anionotropic isomerisation to yield deca-3,7-dien-5-yne-2,9-diol (LXX). When this isomerisation was carried out in an alcoholic solution of sulphuric acid, 2,9-diethoxydeca-3,7-dien-5-yne (LXXI) was obtained:



Quite recently Yanovskaya and Kucherov[187] obtained 2,6-dimethylhepta-2,6-dien-4-yn-1-al (LXXII) in 20% yield by condensation of β-ethoxy-α-methylacrolein with isopropenylethynyllithium in ethereal solution followed by hydrolysis of the product with acetic acid in the presence of sodium acetate:



‡ See formula (XXIX) on p.249 (Ed. of Translation).

1. I.N.Nazarov, Uspekhi Khim., 20, 71 (1951).
2. G.Mignonac, R.de Saint-Aunay, Compt.rend., 188, 959 (1929).
3. J.A.Nieuwland, W.S.Calcott, F.B.Downing, and A.S.Carter, J.Amer.Chem.Soc., 53, 4197 (1931).
4. I.G.Farbenindustrie A.-G., French P. 79242; Chem.Abs., 30, 4240 (1936).
5. I.G.Farbenindustrie A.-G., B.P. 438546; Chem.Abs., 30, 2669 (1936).
6. Itaru Mitta, J.Chem.Soc.Japan, 64, 633 (1943); Chem. Abs., 41, 3742 (1947).
7. A.S.Carter, U.S.P. 2219379; Chem.Abs., 35, 1064 (1941).

8. A.L.Klebanskii, L.G.Tsurikh, and I.M.Dolgopol'skii, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 191 (1935).
9. W.S.Calcott and F.B.Downing, Canad.P. 368209; Chem. Abs., 31, 7443 (1937).
10. M.Iguchi and G.Hakanishi, Chem.Abs., 43, 3225 (1949).
11. L.G.Tsurikh and A.Ginzburg, Zhur.Obshch.Khim., 5, 1468 (1935).
12. M.Lange, U.S.P. 2237353; Chem.Abs., 35, 4396 (1941).
13. O.Fuchs, U.S.P. 2316536; Chem.Abs., 37, 5808 (1943).
14. Jiro Murata, J.Soc.Chem.Ind., Japan, 47, 199 (1944); Chem.Abs., 42, 6310 (1948).
15. Nippon Carbide Industrial Co., Jap.P. 153480; Chem.Abs., 43, 3023 (1949).
16. Nippon Nitrogenous Fertilizers Co., Jap.P. 158552; Chem. Abs., 44, 2011 (1950).
17. W.E.Jones and R.L.Barker, B.P. 628731; Chem.Abs., 44, 2543 (1950).
18. E.N.Martinson and N.I.Kobozev, Zhur.Fiz.Khim., 21, 85 (1947).
19. H.Schmitz and H.Schumacher, Z.Elektrochem., 45, 503 (1939).
20. E.I.du Pont de Nemours and Co., B.P. 733663; Chem.Abs., 27, 1011 (1933).
21. F.B.Downing, A.S.Carter, and D.Hutton, U.S.P. 1926039; Chem.Abs., 27, 5755 (1953).
22. I.G.Farbenindustrie A.-G., B.P. 486918; Chem.Abs., 32, 8633 (1938).
23. A.Wolfram, H.Jockusch, and A.Perlick, U.S.P. 2227478; Chem.Abs., 35, 2532 (1941).
24. I.G.Farbenindustrie A.-G., B.P. 450761; Chem.Abs., 31, 186 (1937).
25. R.Stadler and A.Auerhahen, German P. 639242; Chem. Abs., 31, 1431 (1937).
26. I.G.Farbenindustrie A.-G., French P. 798309; Chem.Abs., 30, 7127 (1936).
27. L.G.Tsurikh, E.Efimova, V.Bartashev, and Yu.Yanits, Zhur.Obshch.Khim., 6, 197 (1936).
28. Ammonia Casale Soc.Anon., French P. 797935; Chem. Abs., 30, 7121 (1936).
29. I.G.Farbenindustrie A.-G., French P. 797642; Chem.Abs., 30, 7120 (1936).
30. H.Berg, H.Heim, and F.Leiss, U.S.P. 2222394; Chem. Abs., 35, 1807 (1941).
31. A.Wacker, French P. 824453; Chem.Abs., 5858 (1938).
32. A.S.Carter and F.B.Downing, U.S.P. 2282705; Chem. Abs., 36, 5832 (1942).
33. Nippon Mining Co., Jap.P. 156472; Chem.Abs., 44, 3002 (1950).
34. W.H.Carothers and R.A.Jacobson, J.Amer.Chem.Soc., 55, 1097 (1933).
35. R.Lespieau and Guillemonat, Compt.rend., 195, 245 (1932).
36. Zh.I.Iotsich, Zhur.Russ.Fiz.-Khim.Obshch., 43, 681 (1911).
37. I.I.Zaretskaya and I.N.Nazarov, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 529 (1946).
38. I.N.Nazarov and L.I.Pinkina, Zhur.Obshch.Khim., 18, 681 (1948).
39. I.N.Nazarov and L.I.Pinkina, Zhur.Obshch.Khim., 18, 675 (1948).
40. I.N.Nazarov and I.V.Torgov, Zhur.Obshch.Khim., 18, 1338 (1948).
41. I.N.Nazarov and S.A.Vartanyan, Zhur.Obshch.Khim., 21, 374 (1951).
42. I.N.Nazarov and M.S.Burmistrova, Zhur.Obshch.Khim., 20, 1304 (1950).
43. I.N.Nazarov and S.A.Vartanyan, Zhur.Obshch.Khim., 20, 1582 (1950).
44. S.A.Vartanyan and V.N.Zhamagortsyan, "Sbornik Statei po Obshchei Khimii" (Collected Papers on General Chemistry), Vol.2, Izv.Akad.Nauk SSSR, 1953, p.963.
45. S.A.Vartanyan and V.N.Zhamagortsyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 12, 45 (1959).
46. S.A.Vartanyan and V.N.Zhamagortsyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 11, 101 (1958).
47. I.N.Nazarov, A.I.Kuznetsova, and I.A.Gurevich, Zhur. Obshch.Khim., 20, 376 (1950).
48. A.M.Blomquist and C.S.Marvel, J.Amer.Chem.Soc., 55, 1655 (1933).
49. P.S.Pinkney, G.A.Nesty, R.H.Wileyand, and C.S.Marvel, J.Amer.Chem.Soc., 58, 972 (1936).
50. D.T.Mitchell and C.S.Marvel, J.Amer.Chem.Soc., 55, 4276 (1933).
51. C.S.Marvel, R.Mozinga, and R.White, J.Amer.Chem.Soc., 62, 1880 (1940).
52. G.Dupont, Compt.rend., 152, 197 (1911).
53. Yu.S.Zalkind and Z.V.Smagina, Zhur.Obshch.Khim., 7, 470 (1937).
54. G.A.Nesty and C.S.Marvel, J.Amer.Chem.Soc., 59, 2662 (1937).
55. P.S.Pinkney and C.S.Marvel, J.Org.Chem., 7, 88 (1939).
56. P.S.Pinkney and C.S.Marvel, J.Amer.Chem.Soc., 59, 2669 (1937).
57. C.S.Marvel and L.A.Patterson, J.Amer.Chem.Soc., 63, 2218 (1941).
58. C.S.Marvel, R.Mozinga, and E.S.Kirkpatrick, J.Amer. Chem.Soc., 61, 2003 (1939).
59. P.S.Pinkney, G.A.Nesty, D.E.Pearson, and C.S.Marvel, J.Amer.Chem.Soc., 59, 2666 (1937).
60. Yu.S.Zalkind and N.I.Shuvalov, Zhur.Obshch.Khim., 7, 1235 (1937).
61. A.T.Babayan, Zhur.Obshch.Khim., 9, 1410 (1940).
62. A.D.Petrov and L.D.Korlik, Zhur.Obshch.Khim., 11, 1100 (1941).
63. V.N.Krestinskii and N.I.Summ, Zhur.Obshch.Khim., 7, 440 (1937).
64. K.Meyer and K.Schuster, Ber., 55, 819 (1922).
65. G.Dupont, Annalen, 30, 512 (1913).
66. H.I.Marsel, U.S.P. 2949493.
67. J.A.Nieuwland and R.Vogt, "The Chemistry of Acetylene" (Translated into Russian), Inostr.Lit., 1947, p.260.
68. E.I.du Pont de Nemours and Co., French P. 733681; Chem.Zentr., I, 1852 (1933).
69. M.S.Badollet, U.S.P. 2040818; Chem.Abs., 30, 4526 (1936).
70. A.L.Klebanskii, Kauchuk i Rezina, 1 (4Ya), 16 (1937).
71. Zh.A.Volim and I.S.Morozov, USSR P. 42049; Chem. Zentr., II, 1959 (1934).
72. A.M.Collins, U.S.P. 2078194; Chem.Abs., 31, 4421 (1937).
73. A.M.Collins, U.S.P. 2008746; Chem.Abs., 29, 6084 (1935).
74. A.M.Collins, U.S.P. 366160; Chem.Abs., 31, 5067 (1937).
75. G.W.Rigby, U.S.P. 2110699; Chem.Abs., 32, 3426 (1938).
76. E.Rodmann, U.S.P. 2036300; Chem.Abs., 30, 3668 (1936).
77. P.V.Zhavoronkov, A.P.Alekhin, and R.S.Shteren, Prom. Org.Khim., 2, 219 (1936).
78. H.P.Hayden, Ind.Eng.Chem., 24, 563 (1932).
79. H.P.Hayden, Ind.Eng.Chem., 25, 1219 (1933).
80. W.S.Calcott, F.B.Downing, and S.Powers, U.S.P. 1829502; Chem.Zentr., I, 1841 (1932).
81. W.S.Calcott, A.S.Carter, and F.B.Downing, U.S.P. 1959343; Chem.Abs., 28.
82. W.S.Calcott, A.S.Carter, and F.B.Downing,

U.S.P. 1959408; Chem.Abs., 28.
83. W.S.Starkweather, J.Amer.Chem.Soc., 56, 1870 (1934).
84. E.I.du Pont de Nemours and Co., B.P. 384655.
85. B.I.Humphrey, Canad.P. 371143; Chem.Abs., 32, 2783 (1938).
86. W.H.Carothers, U.S.P. 2061018; Chem.Abs., 31, 781 (1937).
87. French P. 787562; Chem.Abs., 30, 1151 (1936).
88. B.Johnson, Canad.P. 366034; Chem.Abs., 31, 5218 (1937).
89. Standard Oil Development Co., French P. 787577; Chem. Abs., 30, 1224 (1936).
90. P.I.Wiezevich, Canad.P. 365654; Chem.Abs., 31, 4492 (1937).
91. Standard Oil Development Co., French P. 812490; Chem. Abs., 32, 1138 (1938).
92. W.Wilke, R.Stadler, and E.Lappe, U.S.P. 2208308; Chem.Abs., 30, 1543 (1936).
93. H.Cupery and W.H.Carothers, J.Amer.Chem.Soc., 56, 1167 (1934).
94. A.L.Klebanskii, M.Elnevskii, and V.Chugunov, Zhur. Obshch.Khim., 17, 1436 (1947).
95. M.Tuot and M.Guyard, Compt.rend., 225, 809 (1947).
96. T.Komada, J.Chem.Soc.Japan, 63, 949 (1947); Chem. Abs., 41, 3743 (1947).
97. M.Katake and R.Fukui Terachima, J.Chem.Soc.Japan, 65, 423 (1944); Chem.Abs., 41, 3742 (1947).
98. W.S.Calcott, U.S.P. 2156936; Chem.Abs., 33, 6349 (1939).
99. V.I.Isagulyants, G.T.Esayan, A.G.Terzyan, R.M.Oganesyan, and N.M.Manasaryan, Dokl.Akad.Nauk SSSR, 94, 883 (1954).
100. W.H.Carothers and D.D.Coffman, J.Amer.Chem.Soc., 55, 2040 (1933).
101. A.N.Akopyan and V.S.Aslamazyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 13, 155 (1960).
102. A.N.Akopyan and G.Gabrielyan, Izv.Akad.Nauk Armyansk. SSR, Khim.Nauki, 13, 165 (1960).
103. W.H.Carothers, J.Amer.Chem.Soc., 55, 2008 (1933).
104. I.N.Nazarov and I.I.Zaretskaya, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 211 (1941).
105. D.B.Killian, G.F.Hennion, and J.A.Nieuwland, J.Amer. Chem.Soc., 58, 892 (1936).
106. W.H.Carothers and R.A.Jacobson, U.S.P. 2013725; Chem.Abs., 29, 6903 (1935).
107. A.L.Klebanskii, D.M.Krasinskii, and L.G.Safronovoa, Zhur.Obshch.Khim., 16, 1213 (1946).
108. A.L.Klebanskii, D.M.Krasinskii, and L.G.Safronovoa, Zhur.Obshch.Khim., 16, 1231 (1946).
109. S.A.Vartanyan and Sh.O.Badanyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 11, 343 (1958).
110. S.A.Vartanyan and Sh.O.Badanyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 13, 141 (1960).
111. A.A.Petrov, V.A.Kormer, and T.V.Yakovleva, Zhur. Obshch.Khim., 30, 2239 (1960).
112. A.L.Klebanskii, L.V.Petrov, and N.Ya.Tsukerman, Zhur. Obshch.Khim., 16, 2082 (1946).
113. A.A.Petrov and Yu.I.Porfir'eva, Zhur.Obshch.Khim., 30, 1818 (1960).
114. S.A.Vartanyan, V.N.Zhamagortsyan, and A.O.Tosunyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 14, 139 (1961).
115. S.A.Vartanyan, A.O.Tosunyan, and L.G.Mesropyan, Izv. Akad.Nauk Armyansk.SSR, Khim.Nauki, 16, 137 (1963).
116. A.A.Petrov and Yu.I.Kheruze, Zhur.Obshch.Khim., 33, 1111 (1963).
117. D.D.Coffman, J.A.Nieuwland, and W.H.Carothers, J.Amer.Chem.Soc., 55, 2048 (1933).
118. A.E.Akopyan, Zhur.Prikl.Khim., 27, 639 (1954).
119. I.N.Nazarov and Ya.I.Yanbikov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 43 (1943).
120. I.N.Nazarov and Ya.I.Yanbikov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 66 (1942).
121. I.N.Nazarov, Yu.I.Yanbikov, and I.V.Kuvarzina, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 135 (1942).
122. I.N.Nazarov, Uspekhi Khim., 14, 1 (1945).
123. I.N.Nazarov, A.I.Kakhniashvili, and V.F.Ryabchenko, "Sbornik Statei po Obshchei Khimii" (Collected Papers on General Chemistry), Vol.II, 1953, p.913.
124. S.A.Vartanyan, Sh.O.Badanyan, and G.A.Musakhanyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 16 (1963).
125. I.N.Nazarov and Ya.I.Yanbikov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 389 (1943).
126. S.A.Vartanyan and A.O.Tosunyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 11, 415 (1958).
127. I.M.Malenok, S.D.Kul'kina, and Z.Yu.Kovrushenko, Zhur. Obshch.Khim., 28, 428 (1958).
128. I.M.Malenok and S.D.Kul'kina, Zhur.Obshch.Khim., 25, 1462 (1955).
129. I.M.Malenok and S.D.Kul'kina, Zhur.Obshch.Khim., 24, 1837 (1954).
130. I.L.Kotlyarevskii, A.S.Zanina, and V.G.Linovich, Izv. Vost.Fil.Akad.Nauk SSSR, 90 (1957).
131. I.L.Kotlyarevskii and A.S.Zanina, Zhur.Prikl.Khim., 30, 1719 (1957).
132. I.L.Kotlyarevskii and A.S.Zanina, Zhur.Prikl.Khim., 30, 1357 (1957).
133. I.L.Kotlyarevskii, A.S.Zanina, and V.G.Linovich, Zhur. Prikl.Khim., 30, 321 (1957).
134. I.L.Kotlyarevskii, L.B.Fisher, A.S.Zanina, M.P.Torpugova, A.N.Volkov, and M.S.Shvartsberg, Izv.Vys. Shkoly, 2, 608 (1959).
135. I.L.Kotlyarevskii and M.S.Shvartsberg, Zhur.Obshch. Khim., 29, 2639 (1959).
136. I.L.Kotlyarevskii and A.S.Zanina, Zhur.Obshch.Khim., 31, 3206 (1961).
137. A.W.C.Taylor, D.C.Jones, and M.L.Noble, B.P. 702360.
138. A.W.C.Taylor, D.C.Jones, and M.L.Noble, B.P. 702332.
139. A.W.C.Taylor, D.C.Jones, and M.L.Noble, B.P. 700187; Chem.Abs., 49, 1790 (1955).
140. R.P.Linstead and A.Z.Wolpole, J.Chem.Soc., 842 (1939).
141. L.K.Evans and A.E.Gillan, J.Chem.Soc., 818 (1941).
142. R.B.Woodword, J.Amer.Chem.Soc., 64, 76 (1942).
143. H.Boston, R.E.Davis, and L.W.Butz, J.Amer.Chem.Soc., 65, 973 (1943).
144. C.S.Marvel, D.E.Pearson, and L.A.Patterson, J.Amer. Chem.Soc., 62, 2659 (1940).
145. I.N.Nazarov and G.P.Verkholetova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 277 (1947).
146. I.N.Nazarov and G.P.Verkholetova, Zhur.Obshch.Khim., 18, 1083 (1948).
147. I.N.Nazarov and S.S.Bakhmutskaya, Zhur.Obshch.Khim., 19, 1177 (1949).
148. M.Levitz, F.Perelman, and M.Bogert, J.Org.Chem., 6, 105 (1941).
149. R.P.Linstead and W.E.Doering, J.Amer.Chem.Soc., 64, 1991 (1942).
150. J.E.Gowan and T.S.Wheeler, "Name Index of Organic Reactions", Longman, London, 1960.
151. I.N.Nazarov, I.I.Zaretskaya, Z.N.Parnes, and D.N.Kursanov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 519 (1953).
152. I.N.Nazarov and I.I.Zaretskaya, Zhur.Obshch.Khim., 27, 624 (1957).
153. A.J.Shidlovskaya, Ya.K.Syrkin, and I.N.Nazarov, Dokl. Akad.Nauk SSSR, 94, 905 (1954).
154. I.N.Nazarov and I.I.Zaretskaya, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 194 (1949).

155. I.N.Nazarov and I.L.Kotlyarevskii, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 293 (1949).
156. I.N.Nazarov and I.L.Kotlyarevskii, Zhur.Obshch.Khim., 20, 1949 (1950).
157. I.N.Nazarov and I.I.Zaretskaya, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 184 (1949).
158. I.N.Nazarov and I.I.Zaretskaya, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 200 (1942).
159. I.N.Nazarov and S.A.Vartanyan, Zhur.Obshch.Khim., 20, 1829 (1950).
160. I.N.Nazarov and I.I.Zaretskaya, Zhur.Obshch.Khim., 18, 665 (1948).
161. I.N.Nazarov and L.P.Pinkina, Zhur.Obshch.Khim., 18, 675 (1948).
162. I.N.Nazarov and M.S.Burmistrova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 51 (1947).
163. I.N.Nazarov and M.S.Burmistrova, Zhur.Obshch.Khim., 20, 2173 (1950).
164. I.N.Nazarov and S.S.Bakhmutskaya, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 205 (1947).
165. I.N.Nazarov and M.S.Burmistrova, Zhur.Obshch.Khim., 20, 2021 (1950).
166. I.N.Nazarov and M.S.Burmistrova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 353 (1947).
167. I.N.Nazarov and M.S.Burmistrova, Zhur.Obshch.Khim., 20, 1837 (1950).
168. I.N.Nazarov and L.P.Pinkina, Zhur.Obshch.Khim., 19, 1870 (1949).
169. I.N.Nazarov, S.A.Vartanyan, and S.G.Matsoyan, Zhur. Obshch.Khim., 28, 2758 (1958).
170. I.N.Nazarov, V.M.Romanov, and M.V.Kuvarzina, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 236 (1948).
171. I.N.Nazarov and V.A.Rudenko, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 610 (1948).
172. I.N.Nazarov, A.I.Kuznetsova, and I.A.Gurevich, Zhur. Obshch.Khim., 19, 2148 (1949).
173. I.N.Nazarov and A.I.Kuznetsova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 431 (1941).
174. I.N.Nazarov and F.I.Gotman, Izv.Akad.Nauk SSSR, Otd. Khim.Nauk, 545 (1941).
175. S.A.Vartanyan, S.K.Vardapetyan, and Sh.O.Badanyan, Izv.Akad.Nauk Armyansk.SSR, Khim.Nauki, 13, 251 (1960).
176. C.T.Handy and R.E.Benson, J.Org.Chem., 27, 39 (1962).
177. L.W.Butz, A.M.Garddis, W.J.Butz, and R.E.Davis, J.Org.Chem., 5, 579 (1940).
178. L.M.Joshel, W.J.Butz, and J.Feldman, J.Amer.Chem. Soc., 63, 3348 (1941).
179. L.W.Butz and L.M.Joshel, J.Amer.Chem.Soc., 64, 1311 (1942).
180. W.Nudenberg and L.W.Butz, J.Amer.Chem.Soc., 65, 2059 (1943).
181. L.W.Butz and L.M.Joshel, J.Org.Chem., 7, 199 (1942).
182. L.W.Butz, A.M.Garddis, W.J.Butz, and R.E.Davis, J.Amer.Chem.Soc., 62, 995 (1940).
183. L.W.Butz and L.M.Joshel, J.Amer.Chem.Soc., 63, 3344 (1941).
184. H.H.Inhoffen, O.Isler, G.Bey, *et al.*, Annalen, 580, 7 (1953).
185. P.Milgner and B.C.Weedon, J.Chem.Soc., 3294 (1953).
186. I.M.Heilbron, E.R.Jones, and B.C.Weedon, J.Chem.Soc., 81 (1945).
187. L.A.Yanovskaya and V.F.Kucherov, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 674 (1962).

Institute of Organic Chemistry,
Academy of Sciences of the
Armenian SSR

U.D.C. 541.128.1 : 541.128.3

THE MULTIPLET THEORY OF CATALYSIS — ENERGY FACTORS IN CATALYSIS

A. A. Balandin

CONTENTS

1. Fundamental equations of the multiplet theory 258
2. Bond energies 261
Thermochemical method 261
Comparative method 261
System of Q values adopted 261
Kinetic method 262
3. Effect of extraindicial atoms 264
Hydrogenolysis on nickel 264
Hydrogenolysis on carbon 265
Furan derivatives 265
Hydrogenation of triptycene derivatives 266
Hydrogenation of peroxides and hydroperoxides 266
Effect of substitution within the indicial group — general case 267
4. Effect of intraindicial substituents 267
Hydrogenation of monosaccharides 268
Strain in rings 268
Effect of conjugation energy 268
5. Effect of nature of catalyst 269
6. Effect of environment of active centre 270

An earlier review[1] has surveyed work on the principle of structural correspondence in the multiplet theory of catalysis. However, this principle alone is insufficient according to the theory. Thus ThO_2 and CaF_2 have the same structure, but different catalytic effects on alcohols[2]. A second principle which follows from the multiplet theory — that of energetic correspondence — will be examined below.

1. FUNDAMENTAL EQUATIONS OF THE MULTIPLET THEORY

Spatial (structural) and energetic factors in catalysis are linked by potential-energy curves. Fig. 1 shows such a curve for the chemisorption of an atom A on the surface of a catalyst K. The x axis is taken to pass through the centre of the sorbed atom A and be normal to the plane of the catalyst surface KK. On the atomic scale the profile of the surface is represented by the wavy line ZZ. The adsorbed atom A will be in a more stable position in the trough K' between the surface atoms[1]. In Fig. 1, therefore,