α-Haloacetylene and Diacetylene Alcohols

A. N. Volkov and K. A. Volkova

Faworsky Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, 664033 Russia

Abstract—Results of investigations of α-haloacetylene and diacetylene alcohols in reactions with various reagents are discussed. Frequently the reactions do not stop at monoadduct formation but are followed by intramolecular cyclization or by rearrangement providing polyfunctional compounds.

INTRODUCTION

Within the last decade a growing importance of α-haloacetylene alcohols in the synthesis of highly complex structures was observed, especially in the chemistry of natural compounds [1]. For instance, the synthesis of some pheromones was possible due to the preparation of 1-bromo- and 1-iodoalkynes which easily underwent unsymmetrical coupling [2]. Ten-stage synthesis of a racemic form of 3(Z),11(S)-dodecen-11-olide ("Ferrulactone II") was based on the coupling of 4-pentyn-2-ol with 3-bromo-2-propyn-1ol with further

Volkov Anatolii Nikolaevich was born in Irkutsk in 1932. Graduated from the Chemical Faculty of Irkutsk State University in 1955. Prosessor on the Chair of Chemistry at Irkutsk State University, Doctor of Chemical Sciences since 1980, published over 230 papers.

The field of scientific interest: reactivity of acetylene and diacetylene compounds.

Volkova Kaleriya Aleksandrovna was born in 1948 in Arzamai town, Irkutsk oblast. Graduated from the Chemical Faculty Irkutsk State University in 1973. Senior researcher at Faworsky Irkutsk Institute of Chemistry Siberian Division, Russian Academy of Sciences, Candidate of Chemical Sciences since 1982. Published 88 papers.

building up of the chain using 3-butyn-1-ol. The resulting lactone was obtained in overall yield 9.7% [3]. Proceeding from the 3-bromo-2-propyn-1-ol syntheses of a series of acetylene and diacetylene retinoids was performed [4]. Especially interesting is the application of α-haloacetylene alcohols to the synthesis of diacetylene alcohols and unsymmetrical diacetylene glycols for they are used in various fields of science and engineering. Owing to their high reactivity and availability the acetylene and diacetylene alcohols are a convenient starting material for preparation of new drugs [5], functionally-substituted heterocyclic [6] and unsaturated compounds [7]. For instance, based on diacetylene glycols esters methods were developed for preparation of polymers and Langmuir–Blodgett films composed of crystals of stretched macromolecules with conjugated bonds in the backbone [8]. These polymers possess various valuable properties which determine the fields of their application (nonlinear optics, one-dimensional semiconductors, photosensitive matarisls etc.) [9].

In the published review [10] on α-haloacetylenes the reactivity of α-haloacetylene and diacetylene alcohols is virtually not considered. The present survey fills in this gap giving information on reactions of α-haloacetylene and diacetylene alcohols with various reagents.

REACTIONS AT THE TRIPLE BOND

A characteristic reaction of a triple bond is an addition of nucleophilic reagents. These reactions are impotant for the study of stereo- and regioselective addition of
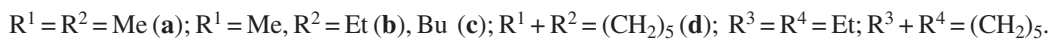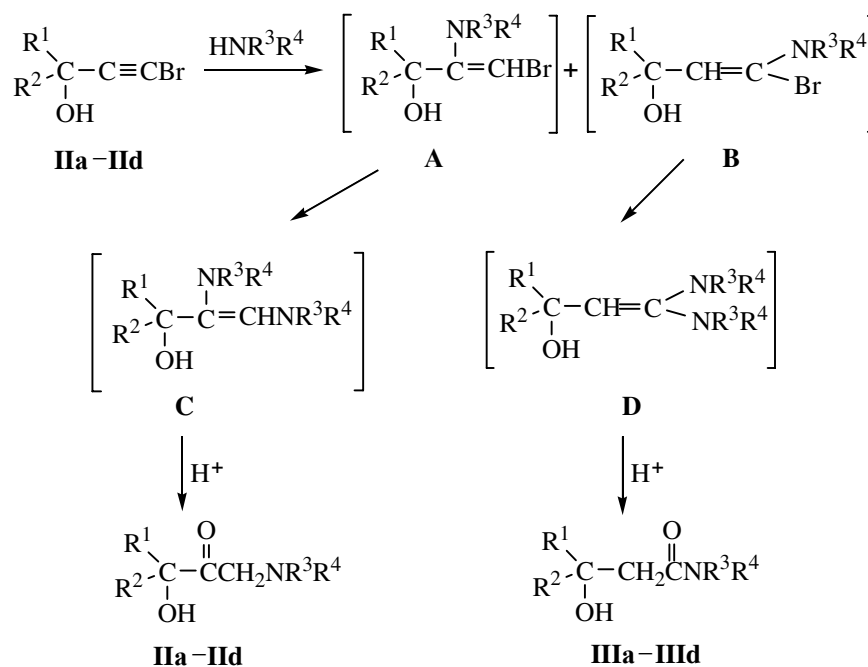
Scheme 1.

$R^1 = R^2 = Me$ (**a**); $R^1 = Me$, $R^2 = Et$ (**b**), Bu (**c**); $R^1 + R^2 = (CH_2)_5$ (**d**); $R^3 = R^4 = Et$; $R^3 + R^4 = (CH_2)_5$.

nucleophilic reagents, and also for the synthesis of versatile classes of olefin and heterocyclic compounds. The nucleophilic attack is facilitated by the presence at the triple bond of an electron-withdrawing substituent [11].

L.I. Vereshchagin studied the addition of secondary aliphatic amines to α-bromoacetylene alcohols **Ia–Id** in benzene or dibutyl ether at heating. The reaction occurred both at the α- and β-carbon of the triple bond apparently through the formation of **A** and **B** intermediates. The subsequent substitution of bromine resulted in **C** and **D** intermediates whose acid hydrolysis gave stable hydroxyaminoketones **IIa–IId** and β-hydroxyacids amides **IIIa–IIId** (Scheme 1) [12].

At the use of piperidine ketones **II** prevail in the hydrolyzate (82–86%), and with diethylamine amides **III** are mainly formed (60–61%). These facts were rationalized in [12] as originating from the steric effect and nucleophilicity of the amine.

With diacetylene alcohols the reaction occurs as addition-elimination and finally results in the formation of a pyran structure. 6-Bromo-2-methyl-3,5-hexadiyn-2-ol (**IV**) in a reaction with excess secondary amine in ether or benzene solution already at room temperature readily gives in high yields the corresponding 1-dialkylamino-diacetylenes **V** [13]. The reaction presumably proceeds

through an intermediate compound **E** with subsequent dehydrobromination into compound **V**. On adding alcohol **IV** to the boiling solution of diethylamine in benzene alongside compound **V** 2,2-dimethyl-4,6-bis(diethylamino)pyran (**VI**) was obtained in 51% yield. The formation of pyran **VI** occurs apparently by an independent route through **F** intermediate containing three amine molecules (Scheme 2).

This scheme of pyran **VI** formation was confirmed by the reaction of alcohol **IV** with propylamine. In this case a crystalline substance was isolated from the reaction mixture corresponding to addition of three propilamine molecules to alcohol **IV** (benzene, 20°C, 15 h). At further heating this crystalline compound was converted into 2,2-dimethyl-*N,N*-dipropyl-2*H*-pyran-4,6-diamine [13]. The cleavage of alcohol **V** by the retro-Faworsky reaction gave *N,N*-dialkylaminobutadiynes which served as starting compounds for the synthesis of ynamines of the diacetylene series [14].
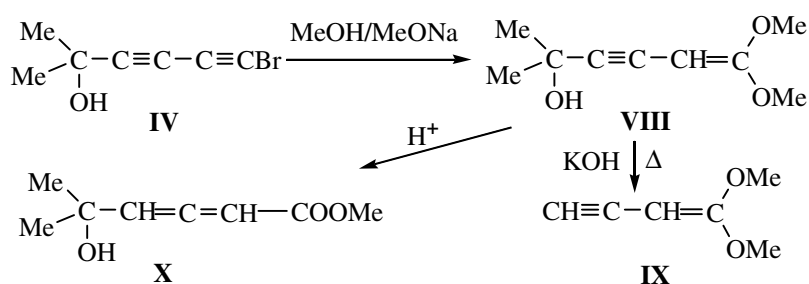
Alcohol **IV** on boiling in methanol with sodium methylate added two molecules of methanol leading to 1,1-dimethoxy-5-methyl-1-hexen-3-yn-5-ol (**VIII**) in 85% yield [15].

Alkaline cleavage of alcohol **VIII** resulted in 1,1-dimethoxy-1-buten-3-yne (**IX**) interesting for the synthesis of functionally substituted acetylene and polyunsaturated

Scheme 2.

$R = Me, Et; R' = Et.$
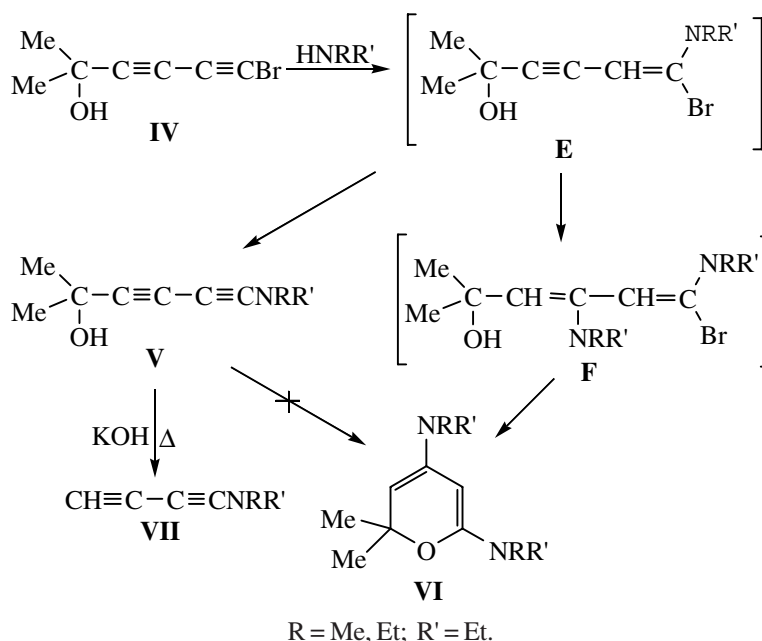
Scheme 3.

structures. In the presence of hydrochloric acid alcohol **VIII** was easily hydrolyzed (20°C, 0.5 h) to methyl 5-hydroxy-5-methyl-2,3-hexadienoate (**X**) (Scheme 3).

Alcohol **IV** under the conditions of acid hydrolysis transformed in good yield into 5-bromomethyl-2,2-dimethylfuran-3-one (**XI**). Allyl bromine is capable to be substituted by amino group giving furanones **XII**, whose reduction with sodium borohydride led to the formation of muscarine analogs **XIII** [16].
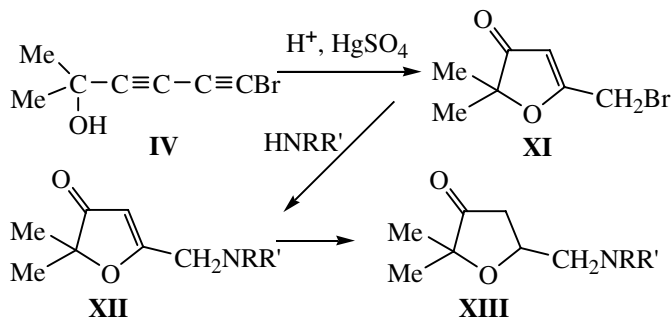
From 6-chloro-3,5-hexadiyn-2-ol by analogous reactions 5-[(dimethylamino)methyl]-2-methyl-3-furanone was obtained, the key compound in the synthesis of muscarine [16].

α-Haloalcohols **XIVa–XIVc** under treatment with bases in anhydrous methanol undergo cyclodimerization into 1,4-dioxanes **XVa–XVc** in 12–40% yield [17].

$X = Cl (\mathbf{a}), Br (\mathbf{b}), I (\mathbf{c}).$
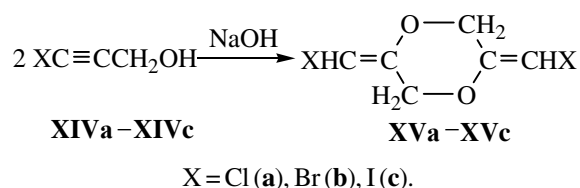
The dimerization rate decreased in the series I, Br, Cl.

1,3-Dipolar addition of benzyl azide to 3-bromo-2-propyn-1-ol **XIVb** was carried out in boiling solvent

(dioxane, toluene, 7 h) and yielded finally 1-benzyl-4-bromo-5-methylol-1,2,3-triazole (**XVI**) [18].


XIVb   **XVI**
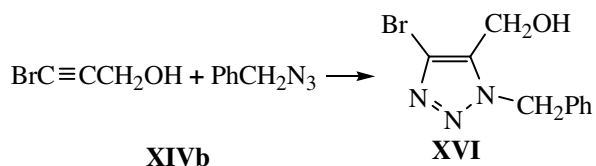
In this case the formation of isomeric 1-benzyl-5-bromo-4-methylol-1,2,3-triazole should be expected, but it was not isolated.

The intermolecular cyclization takes a specific route in the reaction of acetylene and diacetylene alcohols with ketones [11]. A useful information on the reactivity of acetylene alcohols was published in [19]. In the ^{13}C NMR spectra the chemical shifts of ethynyl carbons qualitatively indicate the electron density on the triple bond, and the difference in the chemical shifts $\Delta\delta$ characterizes the polarity of the bond. Introduction of a bromine into the acetylene alcohols contiguous to the triple bond strengthens its polarization thus facilitating the nucleophilic attack on the triple bond. Therefore alcohols **Ia** and **XIVb** actively react with ketones first giving hemiacetal **G** with subsequent intramolecular nucleophilic addition to the triple bond resulting in 1,3-dioxolanes **XVII** formation.


Ia, XIVb   **G**

XVII
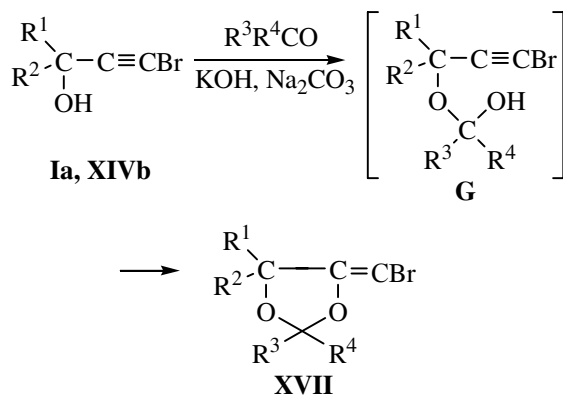
Reaction of alcohols **Ia–Id**, **XIVa**, and **XIVb** with formaldehyde occurred in a similar way [20].

Alcohol **Ia** readily reacted with phenyl isocyanate in the presence of pyridine 18–25°C involving the hydroxy group followed by intramolecular cyclization into


Ia   **XVIII**
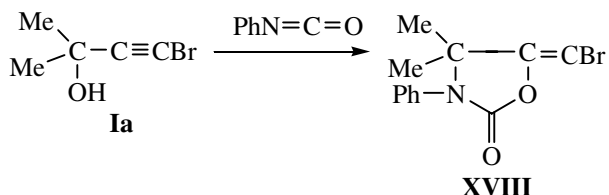
4-bromomethylene-5,5-dimethyl-3-phenyl-2-oxazolidone **XVIII** in 82% yield [21].

The reaction of alcohols **XIVa** and **XIVb** with hypophosphorous acid (**XIX**) occurred in unusual fashion giving halosubstituted propadienephosphonous acids **XXa** and **XX** in up to 67% yield, namely, a hydrophosphoryl acetylene-allene rearrangement was observed [22].

XIVa, XIVb   **XIX**   **XXa, XXb**
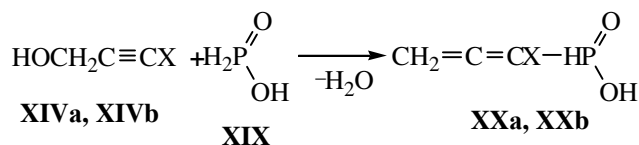
The reaction is carried out by azeotropic distillation of water from the benzene solution of hypophosphorous acid and acetylene alcohol under inert gas atmosphere.

The other example of allene structure formation is the reaction of chloro- bromoacetylene alcohols **XXI** with phenyl- or toluenesulfinyl chloride. In this case the arising sulfinic acids esters **XXII** by a [2,3]-sigmatropic shift transform into halosulfonylallenes **XXIII** [23].


XXI   **XXII**

XXIII

$R^1 = t\text{-Bu, Ph}; R^2 = \text{Ph}; X = \text{Cl, Br}; R^3 = \text{Ph, Tol}$
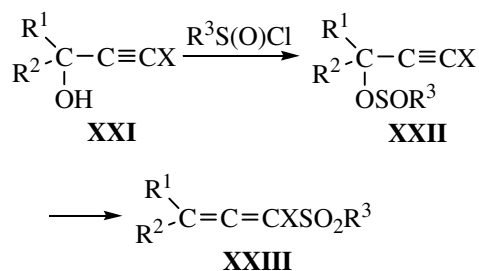
Analogously to chlorosulfonates $ClPR_2^3$ or sulfenyl chlorides R^3SCl phosphorylallenes $R^1R^2C=C=C(X)P(O)R_2^3$ and haloallenesulfoxides $R^1R^2C=C=C(X)S(O)R^3$ were also obtained.

Reaction of alcohols **Ia** and **Ib** with isobutyric aldehyde gave rise to α-bromoallenes **XXIVa** and **XXIVb** in 25–40% yield (Scheme 4) [24].

The reaction was performed in the presence of p-toluenesulfonic acid in a benzene–toluene solution, 1:1, without isolation of intermediate acetals and vinyl propargyl ethers which by Claisen rearrangement gave the final products.

Hydrogenation of alcohol **XIVb** with LiAlH$_4$ in ether in the presence of AlCl$_3$ led to the formation of (*E*)-3-bromo-2-propen-1-of **XXV** that by the coupling with nona-1,8-diyne in the presence of the catalyst [PdCl$_2$(PPh$_3$)$_2$] and CuI in diethylamine (N$_2$, 20°C, 1 h) gave (*E*)-dodeca-

Scheme 4.

Ia, Ib

XXIVa, XXIVb

Scheme 5.

XXV + HC≡C(CH₂)₅C≡CH ⟶ XXVI

XXVII ⟶ XXVIII
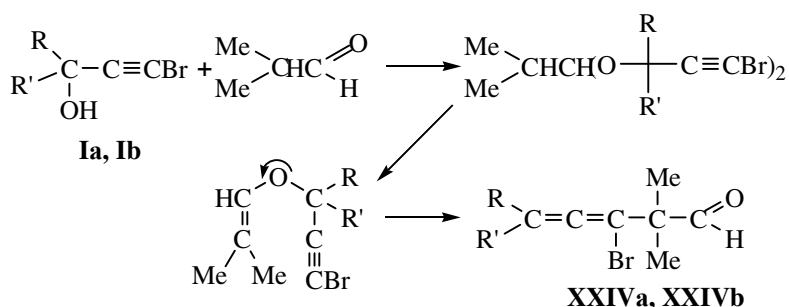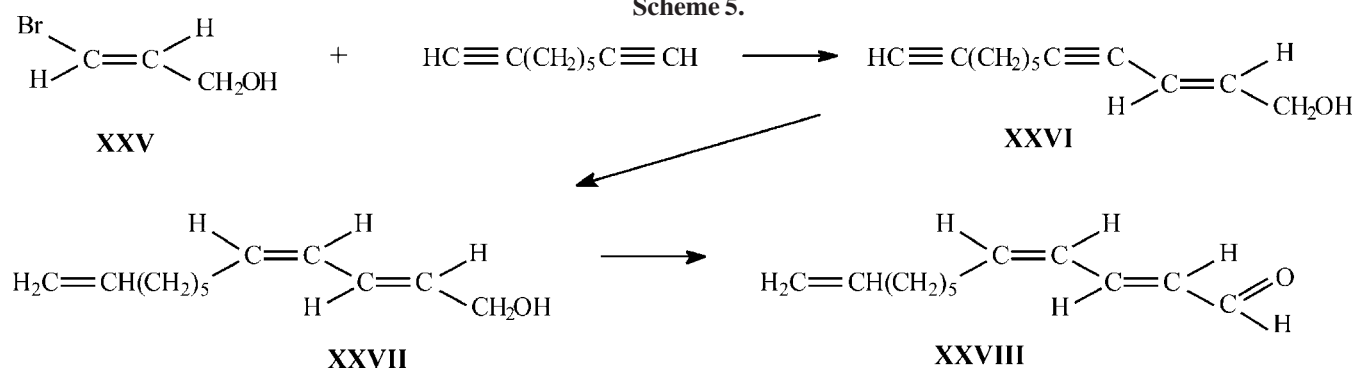
4,11-diyn-2-en-1-ol (**XXVI**) in 65% yield. Hydrogenation of compound **XXVI** in the presence of Lindlar catalyst in anhydrous methanol provided (2*E*,4*Z*)-dodeca-2,4,11-trien-1-ol (**XXVII**) that was oxidized by bipyridinium chlorochromate into (2*E*,4*Z*)-dodeca-2,4,11-trienal (**XXVIII**), the linoleic acid dehydration product (Scheme 5) [7].

From esters of alcohol **XXV** pure enantiomeric aza-sugars were obtained through a series of transformations [25].

The reduction of alcohol **Ia** with a zinc–copper couple (*i*-PrOH–H₂O, KOH, 82°C, 0.5 h) led to the formation of 2-methyl-3-butyn-2-ol in 92% yield [26]. The iodination of alcohols **XIVa–XIVc** in water or methanol solution (20°C, 6 h) resulted in trihaloallyl compounds which acted as repellents of insects [27] and also exhibited fungicidal properties [28].

HALOGEN EXCHANGE REACTIONS

Haloalkynes are relatively inert with respect to nucleophilic substitution [29]. However, the halogen exchange in reactions with organometallic compounds is characteristic of all haloacetylenes [30]. Therefore the reaction of organomagnesium compounds with 4-chloro-2-methyl-3-butyn-2-ol is one among convenient procedures for preparation of tertiary substituted

acetylene alcohols **XXIX** applied to the synthesis of monosubstituted acetylenes **XXX** [31].

The reaction is carried out in ether, THF, or aromatic hydrocarbons. In order to improve the synthesis procedure of compound **XXIX** THF or benzene was replaced by more fire-safe triethylamine [32]. In this case the yield of compound **XXIX** reached 80%.

XXIX XXX

Alk C₃H₇ – C₁₃H₂₇.
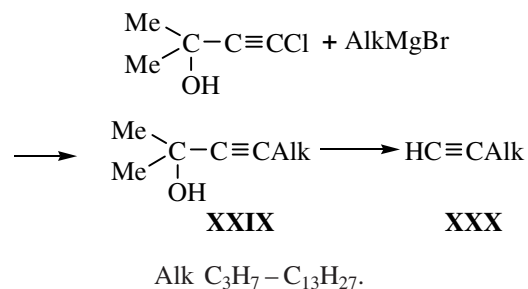
By reaction of 1,1',3-trilithiumrutenocene with 4-iodo-2-methyl-3-butyn-2-ol (THF, –70°C) new ethynyl-substituted rutenocenes were obtained: 1-(3-hydroxy-3-methyl-1-butyne)rutenocene (**XXXI**), 1,1'-bis-(3-hydroxy-3-methyl-1-butyne)rutenocene (**XXXII**), and 1,1',3-tris(3-hydroxy-3-methyl-1-butyne)rutenocene (**XXXIII**) [33].

The cleavage of compound **XXXI** in the presence of KOH led to the formation of 1- ethynylrutenocene, and dehydration (toluene, 100°C, pyridinium *p*-toluene-sulfonate) gave 1-(3-methyl-3-butenyl)rutenocene.
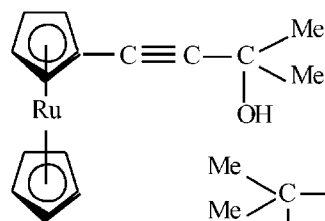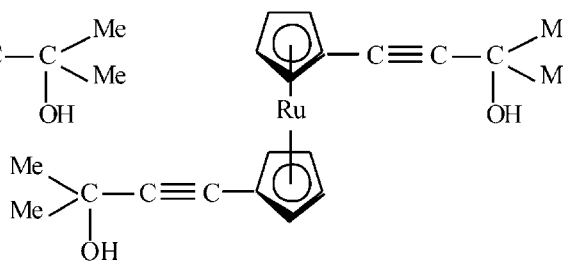
XXXI   **XXXII**   **XXXIII**

CADIOT– CHODKIEWICZ REACTION

The unsymmetrical condensation of acetylene compounds by Cadiot–Chodkiewicz reaction became very important for the synthesis of naturally occurring highly unsaturated unsymmetrical polyacetylenes [34], and also of monomers capable of polymerization in the solid phase [8, 35]. The reaction is possible in the presence of nearly all functional groups in the acetylene compounds involved into the condensation [1, 36, 37]. Often acetylene an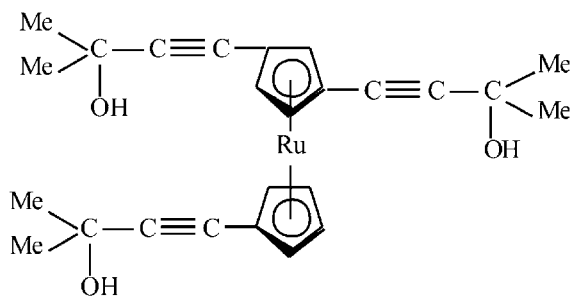d diacetylene alcohols are used as halosubstituted acetylene compounds. The preparation methods for α-haloacetylenes are well known [2, 30, 38]. Note only that relatively recently a method was developed for α-bromoalkynes synthesis (yield > 90%) by treating the terminal acetylenes with triphenylphosphine/tetrabromomethane as brominating agent [39]. In another case [40] α-bromo- and α-iodoacetylenes were obtained by reaction of trimethylsilylacetylene with *N*-bromo- or *N*-iodosuccinimide in the presence of silver nitrate.

In general the condesation of the α-haloacetylene alcohols with terminal acetylenes is carried out in the presence of catalytic quantity of copper chloride dissolved in a primary amine (ethylamine, *n*-butylamine) [41]. To maintain the concentration of copper(I) ions a little amount of reducing agent is added (hydroxylamine hydrochloride), and then the solution of α-haloacetylene in organic solvent is introduced. The general scheme of the reaction consists of two stages:

$$CR \equiv CH + Cu^+ \longrightarrow CR \equiv CCu + H^+;$$

$$CR \equiv CCu + BrC \equiv CR \longrightarrow RC \equiv C - C \equiv CR' + CuBr.$$
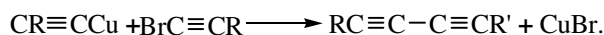
The copper (I) ion concentration should be low (~1%) to avoid the autocondensation of the haloalkyne.

In this manner were prepared, for instance, pyrazolyldiacetylene alcohols [42], diacetylene alcohols, and unsymmetrical diacetylene glycols containing piperidine or pyran rings [43, 44]. The catalytic hydrogenation of these compounds provided the corresponding saturated glycols conserving the conformation of the initial acetylene alcohols.

The condensation of heterocyclic α-bromoacetylene alcohols with various propargylamines led to the formation of diacetylene aminoalcohols endowed with a biological activity [43].

For several years publications appeared on improvements of the primary procedure of Cadiot–Chodkiewicz [1]. However the condensation of bromoalkynes with copper acetylides in boiling pyridine or DMF [45] gives low yields of diynes, and thus the procedure is hardly successful alternative to that of Cadiot–Chodkiewicz. The most efficient catalyst of the unsymmetrical coupling of α-haloalkynes with terminal acetylenes is copper(I) iodide in pyrrolidine [46]. The simplicity and efficiency of this method ensures preparation of the corresponding diacetylene alcohols and glycols in yields up to 98%. In the case of α-bromoalkynes palladium catalyst [PdCl$_2$(PPh$_3$)$_2$] in pyrrolidine was suggested for increasing the yield of final products, for the use of other amines resulted in lower yields. The reaction is favored by application of bromo- or iodo-substituted acetylene alcohols. The latter are more reactive but less available. α-Chloroalkynes have no real practical value due to their low activity [46]. In general the processes of cross- and homocoupling with a carbon–carbon bond formation catalyzed by palladium are widely used in the modern organic chemistry. The numerous examples of these reactions are compiled in a series of reviews [47–49] and in a handbook [50]. All the reactions proceed through a common palladium intermediate RPdXL$_2$ that is formed by oxidative addition of RX to the complex of Pd(0). It was recently established that the homocoupling of 1-iodolkynes in the presence of Pd(0) was an efficient procedure for preparation of symmetric 1,3-diynes [51]. The reaction was carried out in DMF at 20°C under

nitrogen in the absence of salts of copper or other transition metals and without bases thus preventing the oxidative dimerization by the oxygen action. However the reaction mechanism is not completely clear. It can be presumably represented by the following scheme.
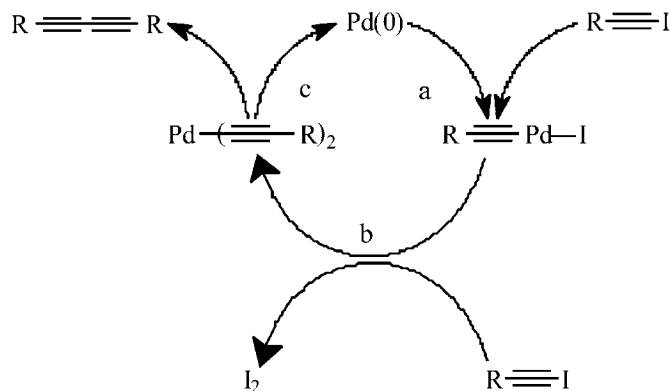
The catalytic cycle includes a stage of an oxidative addition (*a*), transmetallation (*b*) giving diethynylpalladium, and reductive elimination (*c*). It was noted therewith, that the yield of the symmetric 1,3-diyne depended on the character of a substituent in the *para*-position of the benzene ring. In event of electron-donor substituents the yield of 1,3-diynes attained 95%. The cross-coupling of different 1-iodolkynes led to the formation of all three possible 1,3-diynes.

Under catalysis with Pd(0) a reaction of *o*-alkynyl-trifluoroacetanilides with 1-bromoalkynes resulted in formation of 2-substituted 3-alkynylindoles in high yield [52]. The use of 1-iodoalkynes gave worse results for they are prone to homocoupling into 1,3-diynes.

The Cadiot–Chodkiewicz reaction was applied to the synthesis of a series of diyne acids [53]. For instance, the isopalmitic acid (yield 88%) was prepared by unsymmetrical coupling of 4-bromo-2-methyl-3-butyn-2-ol and undecylic acid followed by a catalytic hydrogenation [53]. The unsymmetrical condensation was also successfully applied to preparation of diyne acids esters [53–57]. For instance, methyl dodeca-4,6-diyn-8-olate obtained from 5-bromo-3-methyl-4-pentyl-3-ol and methyl 4-pentynoate was subjected to alkaline cleavage to give methyl hepta-4,6-diyneoate [57], a component of natural polyacetylene compounds [34]. This ester under conditions of the Cadiot–Chodkiewicz reaction readily reacted with various bromoacetylenes providing difficultly aavailable acids of the triacetylene series [57]. Monoesters from hexa-2,4-diyne-1,6-diol and lauric, margaric, and stearic acids exhibit high antimicrobial activity on a par with

levomycetin and streptomycin [55]. The application of diacetylene alcohols bromides appears very promising for the synthesis of endiyne, triyne, and tetrayne compounds [53, 58].

It was observed that at the use of α-bromoacetylene alcohols the yield of the final products was considerably reduced in going from tertiary to primary alcohols [54]. This fact is due to the greater tendency of 3-bromo-2-propyn-1-ol to participate in the side oxidative processes [53].

The interest to acetylene alcohols and glycols as monomers arose after the first publication of Wegner in 1969 [59] on solid-phase polymerization of bis(*p*-toluenesulfonate)hexa-2,4-diyne-1,6-diol. This field of study became promising as a result of the synthesis of quite a number of diacetylene compounds with versatile substituents which polymerized forming crystals or multilayers of various morphology [60]. Recently a significant attention is attracted by the synthesis of amphiphilic bifunctional diynes modified in hydrophilic and hydrophobic parts [9, 61, 62]. In this respect the diacetylene alcohols and glycols obtained by the Cadiot–Chodkiewicz reaction are interesting as bifunctional diynes capable of forming monolayers of high quality and Langmuir–Blodgett films: $RCO_2CH_2(C{\equiv}C)_2CH_2OH$ where R = $C_{13}H_{27}, C_{15}H_{31}, C_{17}H_{35}, C_{21}H_{43}$; yield 51–55% [61]. The important advantage of these films is their thermal and mechanical stability making them applicable in development of new promising technologies [63]. The Cadiot–Chodkiewicz reaction in the synthesis of long-chain diynes results in relatively low yield of the final products, and therefore in some cases another approaches are used, or more active iodoalkynes [9]. Frequently the study of film-forming qualities of amphiphilic diacetylenes is started by the synthesis of diyne acids which are further modified.

The preparation of long-chain terminal diacetylenes is based on the cleavage of tertiary diacetylene alcohols easily obtained by the Cadiot–Chodkiewicz reaction from 4-bromo-2-methyl-3-butyn-2-ol and an appropriate acetylene [56]. These long-chain diynes are capable of stereoregular photopolymerization in ordered structures: microlayers and Langmuir–Blodgett films. In this manner were also obtained aryldiacetylene tertiary alcohols whose cleavage led to the synthesis of terminal aryldiacetylenes containing electron-donor or electron-acceptor substituents in the benzene ring [64, 65]. By polymerization of aryldiacetylenes new photosensitive materials were obtained [65].

Thus in the present review the synthetic opportunities of α-haloacetylene and diacetylene alcohols were demonstrated for preparation of versatile heteroatomic and heterocyclic compounds, and also monomers suitable for application to preparation of materials used in new technology. Further investigations on the reactivity of α-haloacetylene and diacetylene alcohols will provide new data on the mechanism of nucleophilic substitution of a halogen at *sp*-carbon, and will show new ways to the synthesis of practically useful substances.

REFERENCES

 1. Siemsen, P., Livingston, R. C., and Diederich, F., *Angew. Chem., Int. Ed*., 2000, vol. 39, p. 2632.
 2. Hopf, H. and Witulski, B., In *Modern Acetylene Chemistry*, Stang, P.J., Ed., Weinheim: Diederich VCH, 1995, ch. 2, p. 33.
 3. Mavrov, M.V. and Serebryakov, E.P., *Izv. Russian Akad. Nauk, Ser. Khim.,* 1993, p. 2122.
 4. Hopf, H. and Krause, N., *Tetrahedron Lett.,* 1985, vol. 26, p. 3323.
 5. Koreeda, M. and Yang, Wu., *J. Am. Chem. Soc.,* 1994, vol. 116, p. 10793.
 6. Schroth, W., Dunger, S., Billig, F., Spitzner, R., Herzschuh, R., Vogt, A., Jende, T., Isreel, G., and Barche, J., *Tetrahedron,* 1996, vol. 52, p. 12677.
 7. Bohlmann, F. and Rotard, W., *Lieb. Ann.,* 1982, p. 1216.
 8. Misin, V.M. and Cherkashin, M.I., *Usp. Khim*., 1985, vol. 54, p. 956.
 9. Grudinin, A.L. and Domnin, I.N., *Zh. Org. Khim.,* 1996, vol. 32, p. 967.
10. Nakhmanovich, A.S., Komarova, T.N., and Lopyrev, V.A., *Zh. Org. Khim.,* 2000, vol. 36, p. 1599.
11. *Khimiya atsetilenovykh soedinenii* (Chemistry of Acetylenic Compounds), Viie, G.G., Ed., Moscow: Khimiya, 1973, 415 p.
12. Gavrilov, L.D., Mordvina, G.G., Titova, E.I., and Vereshchagin, L.I., *Zh. Org. Khim.,* 1972, vol. 8, p. 2009.
13. Gusev, B.P., Gorlova, E.K., and Kucherov, V.F., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1973, p. 1076.
14. Gusev, B.P., Tsurgozen, L.A., and Kucherov, V.F., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1972, p. 1098.
15. Gusev, B.P., Tsurgozen, L.A., and Kucherov, V.F., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1971, p. 141.
16. Gusev, B.P., Nazarova, I.I., and Kucherov, V.F., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1966, p. 566.
17. Matnishyan, A.A., Grigoryan, S.G., Mkrtchyan, A.A., Kurtikyan, T. S., Ovsepyan, S.A., and Avetisyan, K.G., *Zh. Org. Khim.,* 1982, vol. 18, p. 737.
18. Tikhonova, L.G., Serebryakova, E.S., Maksimova, A.V., Chernysheva, G.V., and Vereshchagin, L.I., *Zh. Org. Khim.,* 1981, vol. 17, p. 1401.
19. Sotnichenko, T.V., Kruglikova, R.I., Varga, M., Vasilenko, I.A., and Unkovskii, B.V., *Zh. Org. Khim.,* 1979, vol. 15, p. 254.
20. Meister, H., *Lieb. Ann*., 1969, vol. 724, p. 128.
21. Kruglikova, R.I., Sotnichenko, T.V., Shingareeva, A.G., and Unkovskii, B.V., *Zh. Org. Khim.,* 1981, vol. 17, p. 649.
22. Belakhov, V.V., Komarov, E.V., and Ionin, B.I., *Zh. Obshch. Khim*., 1987, vol. 57, p. 951.
23. Saalfrank, R.W., Welch, A., Haubner, M., and Bauer, U., *Lieb. Ann*., 1996, p. 171.
24. Mavrov, M.V., Runge, I.S., Rodionov, A.P., and Kucherov, V.F., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1971, p. 883.
25. Polt, R., Sames, D., and Cruma, J., *J. Org. Chem*., 1999, vol. 64, p. 6147.
26. Myaeorg, U., Eelmyae, L., Vyalimyae, T., Khrimyan, A., and Timoteus, Kh., *Izv. Akad. Nauk ESSR, Khimiya*, 1985, vol. 34, p. 270.
27. Morisava, Ya., Konisi, S., and Kataoka, M., Japan Patent 57-99541, 1982; *Ref. Zh. Khim.,* 1983, vol. 190, p. 294.
28. Sasamori, H., Kusu, M., Nizuma, S., Kutsuma, S., and Wakabayashi, A., Japan Patent 12213, 1999; *Chem. Abstr.,* 1999, vol. 130, 164331n.
29. Rybinskaya, M.I., *Zh. Vses. Khim. Obshch*., 1967, vol. 12, p. 11.
30. Smirnov, K.M., Tomilov, A.P., and Shchekotikhin, A.I., *Usp. Khim*., 1967, vol. 36, p. 777.
31. Shchelkunov, S.A., Sivolapova, O.A., Mataev, S.O., Minbaev, D.B., and Muldakhmetov, Z.M., *Zh. Org. Khim.,* 2001, vol. 37, p. 17.
32. Shchelkunov, S.A., Sivolapova, O.A., and Yashkova, N.I., *Zh. Org. Khim.,* 2002, vol. 38, p. 787.
33. Buchmeiser, H. and Schottenberger, H., *J. Organometal. Chem*., 1992, vol. 441, p. 457.
34. Kucherov, V.F., Mavrov, M.V., and Derzhinskii, A.R., *Prirodnye poliatsetilenovye soedineniya* (Natural Polyacetylene Compounds), Moscow: Nauka, 1972, 392 p.
35. Vinogradov, G.A. , *Usp. Khim.,* 1984, vol. 53, p. 135.
36. *Advences in Organic Chemistry*, Intersci. Publisher, 1963.
37. Fisher, L.B. and Shvartsberg, M.S., *Reaktsii atsetilenovykh, soedinenii* (Reactions of Acetylenic Compounds), Novosibirsk: Nauka, 1967, p. 315.
38. Barbu, E. and Tsibouklis, J., *Tetrahedron Lett.,* 1996, vol. 37, p. 5023.
39. Wagner, A., Heitz, M.P., and Mioskowkski, C., *Tetrahedron Lett.,* 1990, vol. 31, p. 3141.
40. Nishikawa, T., Shibuya, S., Hosokawa, S., and Isobe, M., *Synlett.,* 1994, p. 485.
41. Chodkiewicz, W. and Cadiot, P., *C. r*., 1955, vol. 241, p. 1055.
42. Shvartsberg, M.S., Vasilevskii, S.F., Kostrovskii, V.G., and Kotlyarevskii, I.L., *Khim. Geterotsikl. Soedin*., 1969, p. 1055.
43. Praliev, S.D., Sadykov, T., Erzhanov, K.B., and Serikbaev, K.B., *Izv. Akad. Nauk KazSSR, Ser. Khim*., 1986, p. 80; Azerbaev, I.N., Sadykov, T., and Erzhanov, K.B., *Khimiya atsetilena i tekhnologiya karbida kal'tsiya* (Chemistry of Acetylene and Technology of Calcium Carbide), Alma-Ata:

Kazakhstan, 1972, p. 74; Azerbaev, I.N., Erzhanov, K.B., and Bosyakov, Yu.G., *Khim. Geterotsikl. Soedin.,* 1971, p. 623; Azerbaev, I.N., Erzhanov, K.B., Sadykov, T., and Nasonova, A. N., *Izv. Akad. Nauk KazSSR, Ser. Khim.*, 1971, p. 40; Azerbaev, I.N., Erzhanov, K.B., Sadykov, T., Karsybekov, M.A., and Belkhodzhaev, A., *Zh. Org. Khim.,* 1975, vol. 11, p. 205; Azerbaev, I.N., Sadykov, T., Erzhanov, K.B., Karsybekov, M.A., and Belkhodzhaev, A., *Izv. Akad. Nauk KazSSR, Ser. Khim.,* 1974, p. 66.

44. Fei, Y., *Huaxue Shijie*, 1992, vol. 33, p. 247; *Chem. Abstr.*, 1993, vol. 119, 72214w.

45. Curtis, R. F. and Taylor, J. A., *J. Chem. Soc. C.*, 1971, p. 186.

46. Alami, M. and Ferri, F., *Tetrahedron Lett.*, 1996, vol. 37, p. 2763

47. Beletskaya, I.P. and Bumagin, N.A., *Zh. Org. Khim.,* 1996, vol. 32, p. 1771.

48. Negishi, Ei., *J. Organometal. Chem.*, 2002, vol. 653, p.34; Sonogashira, K., *J. Organometal. Chem.*, 2002, vol. 653, p. 46; Nagy, A., Novak, Z., and Kotshy, A., *J. Organometal. Chem.*, 2005, vol. 690, p. 4453.

49. Liang, Bo, Huang, M., You, Z., Xiong, Z., Lu, K., Fathi, R., Chen, J., and Yang, Z., *J. Org. Chem.*, 2005, vol. 70, p. 6097.

50. *Handbook of Organopalladium Chemistry for Organic Synthesis,* Negishi, E., Ed., New York: Wiley & Sons, 2002, vol. 1,p. 2.

51. Damle, S.V., Seomoon, D., and Lee, P.H., *J. Org. Chem.*, 2003, vol. 68, p. 7085.

52. Arcadi, A., Cacchi, S., Fabrizi, G., Marinelli, F., and Parisi, L.M., *J. Org. Chem.*, 2005, vol. 70, p. 6213.

53. Chodkiewicz, W., *Ann. Chim.*, 1957, vol. 13, no. 2, p. 819; Derzhinskii, A.R., Mavrov, M.V., and Kucherov, V.F., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1965, p. 1237; Villemin, D., Cadiot, P., and Kuetegen, M., *Synthesis,* 1984, p. 230; Volkov, A.N., Khudyakova, A.N., Golovanova, N.I., and Shostakovskii, M.F., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1969,

p. 2269; Hear, M.T. W., Jones, E.R.H., Pellatt, M.G., Thaller, V., and Turner, J., *J. Chem. Soc. Perkin 1*, 1973, p. 2785.

54. Chodkiewicz, W., Alhuwalia, J.S., Cadiot, P., and Willemarx, A., *C. r.,* 1957, vol. 245, p. 322.

55. Makhsumov, A.G. and Ergashev, M.S., *Khim.-Farm. Zh.*, 1984, vol. 18, p. 827.

56. Fedenok, L.G., Usov, O.M., and Shvartsberg, M.S., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1995, p. 1525.

57. Azerbaev, I.N., Sarbaev, T.G., Yagudeev, T.A., Urazali-ev, U.I., Khairova, F.Kh., and Dzhakiyaev, G., *Izv. Akad. Nauk KazSSR, Ser. Khim.*, 1973, p. 48.; Derzhinskii, A.R., Mavrov, M.V., and Kucherov, V.F., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1965, p. 544; Ergashev, M.S. and Kasymo-va, S.S., *Uzbek. Khim. Zh.,* 1985, p. 36.

58. Dabdoub, M.J., Baroni, A.C. M., Lenardao, E.J., Gianeti, T.R., and Hurtado, G.R., *Tetrahedron*, 2001, vol. 57, p. 4271.

59. Wegner, G. , *Z. Naturforsch.*, 1969, vol. *B*24, p. 824; *Ref. Zh., Khim.,* 1970, vol. 7*S*, p. 224

60. Arslanov, V.V., *Usp. Khim.*, 1991, vol. 60, p. 1155.

61. Grudinin, A.L., Koshkina, I.M., and Domnin, I.N., *Zh. Org. Khim.,* 1993, vol. 29, p. 1947.

62. Okada, S., Matsuda, H., Otsuka, M., Kikuchi, N., Hayamizu, K., Nakanishi, H., and Kato, M., *Bull. Chem. Soc. Jpn.*, 1994, vol. 67, p. 455; Matsuda, H., Nakanishi, H., Hosomi, T., and Kato, M., *Macromolecules*, 1988, vol. 21, p. 1238.

63. Chechel', O.V. and Nikolaev, E.N., *Usp. Khim.*, 1990, vol. 59, p. 1888.

64. Volkov, A.N., Skvortsov, Yu.M., Danda, I.I., and Shostakovskii, M.F., *Zh. Org. Khim.,* 1970, vol. 6, p. 897; Danda, I.I., Volkov, A.N., and Skvortsov, Yu.M., *Izv. Akad. Nauk SSSR, Ser. Khim.,* 1974, p. 2827.

65. Matsuda, H., Okada, S., Nakanishi, H., Kato, M., Horai, S., and Horiishi, N., Japan Patent 0726223, 1995; *Chem. Abstr.*, 1995, vol. 123, 257768f.