Translated from *Uspekhi Khimii*, **50**, 2049-2072 (1981) U.D.C. 547.412 + 547.311 + 547.312

Copper Salts in Catalytic Reactions of Organic Compounds

Sh.O.Badanyan, M.G.Voskanyan, and Zh.A.Chobanyan

The reactions of copper complexes and organocopper compounds are examined and described systematically. Attention is concentrated on the reactions of copper complexes leading to the formation of carbon-carbon bonds. The influence of various parameters on the mode and mechanism of cuprocatalytic reactions is discussed.
The bibliography includes 343 references.

CONTENTS

I. Introduction 1074
II. Addition reactions 1075
III. Substitution reactions 1077
IV. Alkylation, arylation, and acylation 1078
V. Rearrangements 1078
VI. Dimerisation reactions 1079

I. INTRODUCTION

The study of catalytic processes involving unsaturated systems and the search for ways of their practical utilisation constitute one of the most rapidly developing fields of organic chemistry. Syntheses using catalysts based on copper salts or organocopper compounds are very common[1-12]. By virtue of their unusual and to some extent unique catalytic properties, copper salts have long attracted the attention of many investigators; thus copper(I) chloride is used as the catalyst in numerous important industrial processes—the synthesis of vinylacetylene, acrylonitrile, vinyl chloride, acetaldehyde, etc.

In assessing the reactions occurring in the presence of organocopper catalysts, one may say that they continue to serve as some of the fundamental synthetic methods in modern organic chemistry whereby one can obtain compounds of various classes[8,9,13]. Despite the fact that the first reaction involving organocopper compounds was achieved as early as 1869 by Glaser, the chemistry of these reactions has undergone particular development in the last two decades. Thus, up to the 60's of the present century, only six reactions based on organocopper compounds [reactions (1)–(6)] were known[13-18].

A. Substitution reactions

1. Symmetric oxidative coupling reactions:
(a) the Glaser reaction[15,16]:

$$2RC{\equiv}CCu \xrightarrow{\text{oxidation}} RC{\equiv}CC{\equiv}CR\ ; \quad (1)$$

$$2N{\equiv}CCu \xrightarrow{\text{oxidation}} N{\equiv}CC{\equiv}N\ ; \quad (2)$$

(b) the Ullmann synthesis of biaryls[15,17]:

$$2Ar{-}X \rightarrow Ar{-}Ar\ . \quad (3)$$

2. Asymmetric oxidative coupling reactions:
(a) the Rosenmund synthesis of nitriles[15]:

$$N{\equiv}CCu \xrightarrow{N_2^+Ar} N{\equiv}CAr\ ; \quad (4)$$

(b) the Gattermann synthesis of nitriles[15]

$$N{\equiv}CCu \xrightarrow{N_2^+Ar} NCAr\ . \quad (5)$$

B. Addition reactions

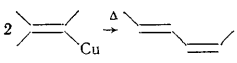
The Straus reactions[18]:

$$RC{\equiv}CCu \xrightarrow{HC{\equiv}CR} RC{\equiv}CCH{=}CHR\ . \quad (6)$$

In the course of the last twenty years a further six new reactions [reactions (7)–(12)] were discovered on their basis[4,5-28].

A. Substitution reactions

1. Symmetrical oxidative coupling reactions:
(a) reactions of vinyl derivatives of organocopper compounds[19-22]:



(7)

(b) oxidative coupling of copper *at*-complexes[23]:

$$[Alk{-}Cu{-}Alk]^-Li^+ \xrightarrow{\text{oxidation}} Alk{-}Alk\ . \quad (8)$$

2. Asymmetric oxidative coupling reactions:
(a) reactions of copper acetylides with aryl halides[5,6,24,25]:

$$RC{\equiv}CCu \xrightarrow{1Ar} RC{\equiv}CAr\ ; \quad (9)$$

(b) synthesis of hydrocarbons from copper *at*-complexes and aryl halides[26]:

$$[CH_3CuCH_3]^-Li^+ \xrightarrow{1Ar} CH_3Ar\ . \quad (10)$$

B. Addition reactions of copper *at*-complexes

(a) Addition to a double bond[27]:

$$[CH_3{-}Cu{-}CH_3]^-Li^+ \xrightarrow{\overset{CO-}{=}} CH_3{-}\underset{|}{\overset{|}{C}}{-}\underset{|}{\overset{|}{C}}{-}CO{-}\ ; \quad (11)$$

(b) addition to a triple bond[28]:

$$[CH_3{-}Cu{-}CH_3]^-Li^+ \xrightarrow{\overset{CO_2CH_3}{=}} \diagdown\!\!=\!\!\diagup_{CO_2CH_3}\ . \quad (12)$$

If we add to the above the fact that organocopper compounds catalyse also the coupling of organomagnesium compounds with various halides[29,30] or the dimerisation of alkyl, alkenyl, or alkynyl groups[29-32] starting with Grignard complexes

$$R{-}MgX \rightarrow R{-}R$$

as well as the use of complex copper salts as oxidants, (Benedict's, Barfoed's, Fehling's, Pavy's, etc. reagents)[33], etc., then the wide spectrum of the action of organocopper complexes and organocopper compounds in organic chemistry will become clear.

Simultaneously with the vigorous research into cuprocatalysis, elegantly written reviews have appeared in recent years in the literature[8-14,17], whose authors discuss mainly the reactions of homo- and hetero-cuprates and devote less attention to the reactions proceedings via organocopper complexes[34-36]. In order to survey the available literature data on numerous reactions with organocopper compounds and copper complexes, in the present review an attempt was therefore made to give a systematic account of the extensive experimental data on reactions involving organocopper complexes; attention is concentrated on the catalytic reactions of unsaturated compounds in the presence of copper salts.

Among organocopper compounds, one usually distinguishes homocuprates, heterocuprates, and copper π-complexes with organic compounds. However, the reactions of copper complexes and cuprates, particularly heterocuprates, are frequently difficult to distinguish from the reactions of pure organocopper compounds. Following the example of many investigators who have already surveyed various aspects of the reactions of organocopper compounds, we shall also consider these reactions together for the sake of convenience and when dictated by necessity.

II. ADDITION REACTIONS

1. Halogenation

A hydrochloric acid solution of copper chlories is an effective chlorinating agent whereby acetylene can be converted into *trans*-dichloroethylene[37-48]. Similarly a mixture of copper(I) and copper(II) bromides brominates acetylene to dibromoethylene[42]. It has been reported[43] that the chlorination reaction also yields 1,1-dichloroethylene[43]. According to certain data, when the chlorination[49,50] as well as the bromination[51] reaction is carried out in less acid media and in the presence of an excess of copper salts, tri- and tetrahalogenoethylenes are formed[49,50,52]:

$$HC{\equiv}CH \rightarrow HCX{=}CX_2\ ;$$
$$HC{\equiv}CH \rightarrow CX_2{=}CX_2\ ;$$
$$X = Cl, \text{ or } Br.$$

Copper(II) halides convert cyanoacetylene almost quantitatively into dihalogenoacrylonitrile[53]:

$$HC{\equiv}CCN \rightarrow HCX{=}CXCN\ ;$$
$$X = Cl \text{ or } Br.$$

A mixture of copper(I) and copper(II) salts was subsequently widely used in the halogenation of vinylacetylene[38,44,54], phenylacetylene[44], diacetylene[54,55], divinylacetylenes[56], as well as acetylenic[57-61] and diacetylenic[62,63] compounds with functional groups. It is remarkable that only the triple bond is then halogenated:

$$RC{\equiv}CH \rightarrow RCX{=}CXH\ .$$

Various workers have frequently dealt with the problem of the elucidation of the mechanism of the halogenation of multiple bonds[3,4,39,57,64-69]; attempts were made to provide an experimental basis for and to relate all the processes occurring in cuprocatalytic solutions[3,4,57,65,70]. However, at present it is impossible to give an exhaustive answer to numerous questions arising in the discussion of the mechanism of these reactions.

The halogenation of acetylene and its derivatives is usually carried out in aqueous or aqueous alcoholic solutions; dimethylformamide (DMF), dioxan, etc. are also used as solvents. However, under analogous conditions alkenes or alkadienes do not interact with bivalent copper salts. Thus it has been shown that the chlorination of butadiene can be achieved only with the aid of copper chloride melts[71-73] or in a fluidised catalyst bed[74]. In all the instances indicated the main reaction products were 3,4-dichlorobut-1-ene and a mixture of *cis*- and *trans*-1,4-dichlorobut-2-enes:

$$CH_2{=}CHCH{=}CH_2 \rightarrow \begin{cases} \rightarrow ClCH_2CH\,(Cl)\,CH{=}CH_2 \\ \rightarrow ClCH_2CH{=}CHCH_2Cl\ . \end{cases}$$

Subsequently it proved possible to halogenate various diolefins by adding various ligands and reducing agents[75-79]. Among these processes, the reaction in which butadiene is converted into a mixture of 1- and 2-chlorobutadienes is of particular interest[75]:

$$CH_2{=}CHCH{=}CH_2 \rightarrow \begin{cases} \rightarrow CH_2{=}CClCH{=}CH_2 \\ \rightarrow ClCH{=}CHCH{=}CH_2\ . \end{cases}$$

Finally, one should note that copper(II) chloride has also been used to halogenate alkenes and cycloalkenes[61]. As was to be expected, this reaction is less successful than for alkynes.

2. Hydrohalogenation and Addition of Hydrocyanic Acid

One of the most important fields of application of copper salts involves their use as catalysts of the hydrohalogenation of acetylene[80] and vinylacetylene[81]:

$$HC{\equiv}CH \xrightarrow{HX} CH_2{=}CHX\ ;$$
$$H_2C{=}CHC{\equiv}CH \xrightarrow{HX} CH_2{=}\underset{X}{C}{=}CHCH_2X \rightarrow$$
$$\rightarrow CH_2{=}\underset{|}{C}CH{=}CH_2\ .$$

Vinyl chloride and chloroprene continue to be synthesised in many countries on the basis of these reactions. Various alkynes, alkenynes, and their derivatives also enter into this reaction. Studies in this field have been frequently discussed and surveyed by various workers[81-83].

It has been found[84] that the triple bond activated by complex copper salts combines with hydrogen cyanide:

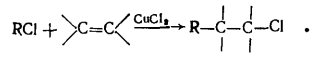
$$RC{\equiv}CH \xrightarrow{HCN} RHC{=}CHCN\ .$$

This method is still one of the most acceptable procedures for the synthesis of acrylonitrile, which is an extremely important monomer and reagent in organic chemistry.

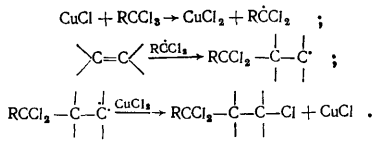
3. The Asscher–Vofsi Addition

Another important application of copper salts involves their use as catalysts of the alkylation of unsaturated systems by organic polyhalogeno-compounds. Thus Asscher and Vofsi[85-87] showed that, in the presence of copper ions, chloroform,

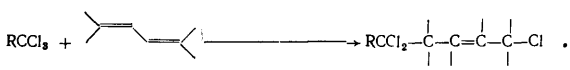
carbon tetrachloride, bromotrichloromethane, and sulphonyl chloride add smoothly to alkenes:



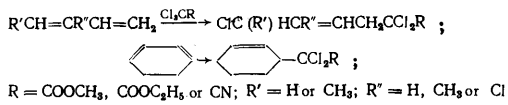
It is of interest that under these conditions a copper(I) salt is an effective catalyst of the chloroalkylation of olefins[88,89], the radical being regenerated via the following mechanism in its presence:



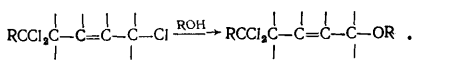
Analogous results have been obtained by other workers in the reaction of alkenes and styrene, on the one hand, and carbon tetrachloride, trichloroacetonitrile, and dichloroacetonitrile, on the other[90-92]. Copper(I) salts have been used successfully also for the halogenoalkylation of various dienes with chloroform, carbon tetrachloride, and bromotrichloromethane[85,88,93]:



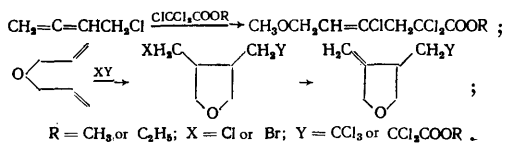
From the preparative point of view, together with the reaction described above, the alkylation of butadiene, isoprene, piperylene, cyclohexadiene, chloroprene, and other halogenodienes with trichloroacetate esters and trichloroacetonitrile in the presence of copper(I) oxide is of considerable interest[94-97]:



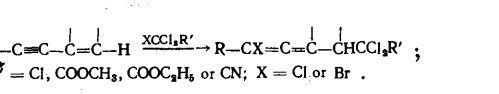
It is remarkable that, when the reaction is carried out in protic solvents, copper(I) salts promote the solvolysis of the allylic halogen generated in the process with formation of an ether[95,96]:



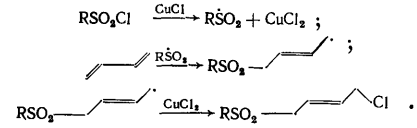
This catalyst has been used successfully for the addition of polyhalogeno-derivatives of organic compounds to cumulated and isolated dienes[94,98]:



It has been shown recently that copper(I) oxide is an effective catalyst of the addition of bromotrichloromethane, trichloroacetate esters, and trichloroacetonitrile to vinyl-, isopropenyl-, and cyclohexenyl-acetylenes and their functional derivatives and satisfactory yields of various allene derivatives have been obtained[94,97,98]:



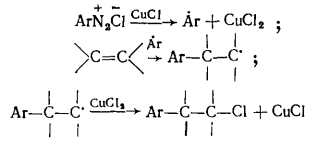
The interaction of various sulphonyl chlorides with dienes also takes place successfully in the presence of copper salts[88,100-103]. The occurrence of the reaction via the following mechanism is usually postulated:



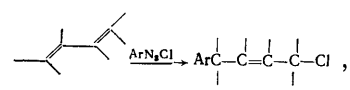
The chlorides of organic sulphonic acids add smoothly under analogous conditions, i.e. in the presence of copper(II) chloride, to vinylacetylenic hydrocarbons[104,105], as well as their silicon-substituted analogues[106,107]. It has been shown that, in the case of hydrocarbons with the normal structure of the enyne residue, the addition is to the double bond whereas in the case of the silicon-containing analogues 1,4-addition is also observed. Thus the Asscher–Vofsi reaction makes it possible to synthesise various organoelemental compounds from ethylene, acetylene, and their derivatives.

4. The Meerwein Arylation

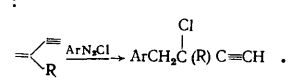
Copper(I) salts have been used successfully in the arylation of alkenes and their derivatives by diazonium chlorides via the Meerwein reaction[108-110]:



Various dienes[109,111], alkynes, enynes[109,112,113] also undergo the Meerwein arylation. Interesting features of the coupled addition of the aryl residue and the halogen to dienes and particularly to enyne systems have been discovered. In the first place one should mention the ability of diazonium salts to arylate conjugated dienes in the 1,4-positions[109,111,113]:



and also the arylation of conjugated enyne compounds at the double bond[81,82,114]:



The characteristics of the reaction associated with the influence of neighbouring groups in unsaturated systems, the presence of substituents in the aromatic ring of diazonium salts, the pH of the medium, the nature of the solvents, the role of the catalyst, etc. are likewise noteworthy and exhaustive information about them can be obtained from elegantly written reviews of the Meerwein reaction[108,109]. It is remarkable that various polyfunctional compounds which are difficult to obtain by othe procedures have been synthesised by the above reaction.

5. The Reppe–Jones Alkynol Synthesis

It has been established that the complex catalyst based on copper salts is effective in the condensation of acetylene with formaldehyde not only under pressure[115-124] but also

without it[124-132]:

$$HC{\equiv}CH \rightarrow HOCH_2C{\equiv}CCH_2OH \ .$$

The reaction takes place more successfully with other aldehydes[115] and with terminal vinylacetylenes[133].

It has been reported quite recently that copper(II) ions catalyse effectively the aldol condensation reaction[134,135]:

$$ArCHO \xrightarrow[Cu^{2+}]{R'CH_2COR} ArCH{=}\overset{R'}{\underset{|}{C}}{-}COR \ .$$

6. Generation of Carbenes

Among cuprocatalytic reactions, the application of complex catalysts based on copper salts in the generation of carbenes is of considerable interest. The characteristic features of the behaviour of the carbenes, obtained in the presence of copper ions, in addition reactions, rearrangements, etc. have been investigated[136-140].

III. SUBSTITUTION REACTIONS

Copper salts have found extensive applications as successful catalysts also in substitution reactions.

1. Solvolytic Reactions

It has been shown[141] that the hydrolysis of allyl chloride is accelerated when a hydrochloric acid solution of copper hemichloride is added to the reaction medium. On the basis of kinetic studies, the authors[141] concluded that the rate of hydrolysis is determined by the stage involving the ionisation of allyl chloride bound in a complex:

$$CuCl + Cl^- \rightarrow \widetilde{CuCl_2} \ ;$$
$$CH_2{=}CHCH_2Cl + CuCl_2^- \rightarrow [CH_2{=}CHCH_2Cl \cdot CuCl_2]^- \ ;$$
$$[CH_2{=}CHCH_2Cl \cdot CuCl_2]^- \rightarrow [CH_2{=}CHCH_2 \cdot CuCl_2] + Cl^- \ ;$$
$$[CH_2{=}CHCH_2CuCl_2] + \overline{OH} \rightarrow CH_2{=}CHCH_2OH + \widetilde{CuCl_2} \ .$$

Continuing the study of the solvolysis of substituted allyl halides in relation to individual stereoisomers, the same workers concluded that the $CuCl_2^-$ ions behave as the catalyst in these reactions[142-144]. The catalytic effect of copper salts on the hydrolysis of allyl chloride in an alkaline medium has also been confirmed in another study[145].

It is noteworthy that another group of investigators demonstrated the possibility, in principle, of the catalysis by copper salts of the reverse reaction, i.e. the formation of allyl chloride from allyl alcohol[146-148]:

$$CH_2{=}CHCH_2OH \xrightarrow[CuCl]{HCl} CH_2{=}CHCH_2Cl \ .$$

2. The Exchange of a Halogen

It has been established recently that copper(I) and copper(II) salts catalyse the exchange of the halogen in allyl halides[149-151]:

$$RR'C{=}CHCH_2Cl \xrightarrow[Cu^+/Cu^{2+}]{HX} RR'C{=}CHCH_2X \ ;$$
$$X = Cl \text{ or } Br.$$

It is of interest that in the case of substituted allyl halides the migration of the reaction centre is observed simultaneously[150]:

$$CH_2{=}CHCCl_3 \rightarrow BrCH_2CH{=}CCl_2 \ ;$$
$$CH_2{=}CHC(Cl)RR' \rightarrow RR'C{=}CHCH_2Br \ .$$

3. Mixed Reactions

Certain examples available at the present time in the literature show that substitution of the allyl chlorine[152] or hydroxyl[153] by a weak nucleophile such as the cyanide ion can also be successfully catalysed by a copper halide:

$$ClCH_2CH{=}CHCH_2Cl \xrightarrow[Cu^{2+}]{KCN} NCCH_2CH{=}CHCH_2CN \xrightarrow[Cu^{2+}]{HCN} HOCH_2CH{=}CHCH_2OH \ .$$

It is striking that, when crotyl chloride is involved in the reaction, dehydrocondensation via the hydrogen atoms of the methyl group takes place simultaneously[154].

Copper salts are likewise effective catalysts of the interaction of the allylic halogen with ammonia and primary and secondary amines[155]:

$$CH_2{=}CHCH_2Cl \xrightarrow[Cu^+/Cu^{2+}]{HNRR'} CH_2{=}CHCH_2NRR' \ ;$$
$$R = H \text{ or Alk}; \ R' = Alk \ .$$

According to patent data[156], copper or its salts can be used as catalysts for the synthesis of unsaturated amines via the mechanism

$$ClCH_2CH(Cl)CH_2Cl \xrightarrow{H_2NR} CH_2{=}C(Cl)CH_2NHR \ .$$

Polyhalogenoalkenes have also been made to react with amines in the presence of copper(II) salts[157]. There have been a number of reports concerning the application of copper(II) salts as catalysts in the reaction of aryl halides with ammonia or amines, leading to the formation of aniline derivatives[158-163].

4. Substitution of the Hydrogen in C–H Acids

(a) For a halogen. According to the available literature data, copper salts promote both the substitution of hydrogen by a halogen in alkanes, aldehydes, and ketones and the dehydrohalogenation of halogenoalkanes[164-173]. They have been used successfully for the synthesis of α-halogenoalkynes from terminal acetylenic compounds[61,174] and for the chlorination of butadienyl sulphone to 1,1,4,4-tetrachlorobuta-1,3-diene.[175]

(b) For dialkylamino-groups. It is also well known that copper salts catalyse the Mannich reaction, in particular the substitution of active acetylenic hydrogen for a dialkylamino-group[176,177]:

$$R{-}C{\equiv}CH \xrightarrow{R'CHO,\ HNR'R''} R{-}C{\equiv}C{-}C(R')HNR'R'' \ .$$

5. The Sandmeyer Reaction

The conversion of diazonium compounds into aryl halides by the substitution of diazo-groups by chlorine via the Sandmeyer reaction, where copper(I) salts are again used as catalysts, can serve as an interesting example of cuprocatalysis[178]. According to Kochi[179], the reaction can be represented schematically as follows:

$$ArN_2Cl \xrightarrow{CuCl} \overset{+}{ArN_2}\widetilde{CuCl_2} \ ;$$
$$\overset{+}{ArN_2}\widetilde{CuCl_2} \rightarrow \dot{A}r + CuCl_2 + N_2 \ ;$$
$$\dot{A}r \xrightarrow{CuCl_2} ArCl + CuCl \ .$$

IV. ALKYLATION, ARYLATION, AND ACYLATION

1. The Colonge–Korts Alkylation

Copper(I) salts are used as catalysts of the alkylation of terminal acetylenes with allyl halides[180–188]:

$$RC{\equiv}CH \xrightarrow{XCH_2C(R'''){=}CR'R''} RC{\equiv}CCH_2C(R'''){=}CR'R''.$$

Allylacetylenes, allylacetylenic alcohols, etc. have been synthesised in this way. A catalytic amount of copper(I) chloride is usually sufficient for the reaction. It is striking that under analogous conditions propargyl chlorides react mainly with inversion of the reaction centre[189,190]:

$$RC{\equiv}CH \xrightarrow{ClCH_2C{\equiv}CH} RC{\equiv}CCH{=}C{=}CH_2 .$$

We may note that allenyl halides with the halogen at an sp^2-hybridised carbon atom enter into this reaction[191]:

$$RC{\equiv}CH \xrightarrow{ClCH{=}C{=}CR'R''} RC{\equiv}CCH{=}C{=}CR'R'' .$$

The alkylation of cyanoacetic ester by propargyl halides in the presence of zerovalent and univalent copper are closely related to the above reaction[192]:

$$HC{\equiv}C{-}\underset{Cl}{\underset{|}{C}}RR' \xrightarrow{NCCH_2CO_2C_2H_5} HC{\equiv}CC(RR')\underset{CN}{\underset{|}{C}}HCO_2C_2H_5 .$$

Finally copper(I) oxide has been used successfully for the alkylation of allylisonitrile with allyl bromide via the mechanism[193]

$$CH_2{=}CHCH_2NC \xrightarrow{BrCH_2CH{=}CH_2} \begin{cases} \rightarrow CH_2{=}CHCH\underset{CN}{\underset{|}{C}}H_2CH{=}CH_2 \\ \rightarrow CH_3CH{=}C{-}\underset{CN}{\underset{|}{C}}H_2CH{=}CH_2 \end{cases} .$$

2. The Sladkov–Castro Arylation, Alkylation, and Acylation

The arylation of ethynylcopper compounds by aryl halides constitutes yet another important field of application of organocopper compounds[5,6,24,25,186,194–197]:

$$RC{\equiv}CCu + ArX \rightarrow RC{\equiv}C{-}Ar ;$$

R = Ar, furyl, etc.; X = I or Br.

Subsequently this method was extended to many classes of organic compounds. Studies in this field have been examined systematically and in detail by Sladkov, Ukhin, and Gol'ding[5,6].

Copper acetylides are smoothly alkenylated by compounds containing an allylic halogen atom[198–200]:

$$RC{\equiv}CCu + XCH_2C(R'){=}CR''R''' \rightarrow RC{\equiv}CCH_2C(R'){=}CR''R''' .$$

Studies by a number of workers have shown that vinyl halides are also capable of reacting with copper acetylides[189, 200,201]; furthermore, the involvement of α-halogenoketones in the above reaction made it possible to develop a fairly convenient method of synthesis of furan derivatives[200]:

$$PhCOCH_2Br \xrightarrow{CuC{\equiv}CR} Ph{-}\langle O \rangle{-}R .$$

The Sladkov–Castro reaction has also been used successfully to synthesise important natural products, particularly pheromones[202]. The reaction of copper acetylides with acid halides shown below is also of interest[199,203]:

$$RC{\equiv}CCu \xrightarrow{R'C(=O)Cl} RC{\equiv}CCOR' .$$

V. REARRANGEMENTS

1. Allyl Halides

The very wide variety of the catalytic properties of copper(I) and copper(II) salts has led to the possibility of using them in the anionotropic rearrangements of unsaturated systems. Such rearrangements are usually characteristic of allyl and propargyl halides. As an illustration, one may quote the isomerisation of 1,4-dichlorobut-2-ene to 1,2-dichlorobut-3-ene in the presence of copper halides on heating[204,205]:

$$ClCH_2CH{=}CHCH_2Cl \rightarrow ClCH_2CH(Cl)CH{=}CH_2 .$$

According to other data[206], 1,4-dichlorobut-2-ene is converted into 1,1-dichlorobut-3-ene under the influence of copper or copper(I) oxide:

$$ClCH_2CH{=}CHCH_2Cl \rightarrow Cl_2CHCH{=}CH_2 .$$

In recent years the synthesis of chloroprene from butadiene has assumed great practical importance. This largely accounts for the attempts by a number of workers to elucidate the possibility of the interconversion of the butadiene chlorination products and to establish their configuration. It was found[207] that, in the presence of copper(I) salts at 35° to 90 °C, an equilibrium mixture of *cis*-1,4-dichlorobut-2-ene (5–6%), *trans*-1,4-dichlorobut-2-ene (70–80%), and 1,2-dichlorobut-3-ene (15–20%) is obtained. Next it was shown that 1,4-dichlorobut-2-ene readily isomerises to 1,2-dichlorobut-3-ene on refluxing in the presence of $CuCl_2$:[208]

$$ClCH_2CH{=}CHCH_2Cl \rightarrow CH_2{=}\underset{Cl}{\underset{|}{C}}HCH_2Cl .$$

One should note particularly that copper naphthenates[209,210] and acetylacetonate[211] have been used as catalysts for the anionotropic isomerisation of allylic halides:

$$CH_3\underset{Cl}{\underset{|}{C}}HCH{=}CH_2 \rightarrow CH_3CH{=}CHCH_2Cl .$$

Cuprocatalysis also occurs in the conversion of 4-chlorobuta-1,2-diene into chloroprene[212]:

$$ClCH_2CH{=}C{=}CH_2 \rightarrow CH_2{=}CClCH{=}CH_2 .$$

2. Propargyl Halides

The conversion of dichlorbutyne into a diene dihalide in the presence of copper(I) chloride and ethylamine hydrochloride in DMF is of great interest[213]:

$$ClCH_2C{\equiv}CCH_2Cl \rightarrow CH_2{=}CClCCl{=}CH_2 .$$

It is known that propargyl halides isomerise to halogenoallenes under the influence of copper(I) salts[214,215]:

$$RR'C{-}\underset{X}{\underset{|}{C}}{\equiv}CH \rightarrow RR'C{=}C{=}CHX ;$$

X = Cl or Br.

When copper salts were used in reactions involving substitution of a hydroxyl for hydrogen in hydrogen halide solutions it was found that, together with acetylenic halides, halogenoallenes are also obtained[216,217]:

$$RR'\underset{OH}{\underset{|}{C}}{-}C{\equiv}CR'' \rightarrow RR'\underset{X}{\underset{|}{C}}C{\equiv}CR + RR'C{=}C{=}\underset{X}{\underset{|}{C}}R'' .$$

A comprehensive study of this reaction showed that allenic compounds are products of the isomerisation of acetylenic halides catalysed by copper salts[216,217]:

$$RR'C(X)-C\equiv CR'' \rightarrow RR'C=C(X)=CR''$$

Studies in this field have been surveyed in reviews by Vartanyan and Badanyan[216], Wotiz[217], and others[218-220], in which the available extensive literature data on this field are examined in detail and described systematically.

3. Rearrangements of Other Systems

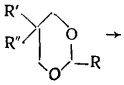
It has been established that copper-based catalysts are used successfully for the rearrangement of α,β-unsaturated alcohols to aldehydes and ketones[221,222]. Here it is important that the latter are formed via the hydrogenation of the intermediate α,β-unsaturated carbinols:

$$RCH=CH-CH(OH)R' \rightarrow RCH=CHCOR' \rightarrow RCH_2CH_2COR' .$$

More detailed data on the anisotropic transformations of alkenes and alkynes can be found in a collection of articles[223] and in a review[218].

In many instances copper complexes are used for prototropic isomerisations[224,225], *cis–trans* transformations[225], the Wolff rearrangement[227], the synthesis of polycyclic compounds[228], the disproportionation of substituted benzenes[229], and for other purposes[230].

Finally one should note the rearrangement of *m*-dioxans to β-alkoxyaldehydes in the presence of copper–silver catalysts[231]:



$$\rightarrow ROCH_2C(R'R'')CHO .$$

VI. DIMERISATION REACTIONS

1. Oxidative Dimerisation

(a) The Glaser and Cadiot–Chodkiewicz oxidative dimerisation of acetylenes. Oxidative coupling reactions of various acetylenes in the presence of copper(I) salts are known in the chemical literature. Here in the first place mention should be made of the Glaser reaction[232] and its modification by Eglinton[238] and also the Cadiot–Chodkiewicz method[234,235] whereby asymmetrically substituted diacetylenes can be obtained.

Recently studies in this field have been surveyed by Eglinton and McCrae[236,237] and other workers[238,239]. The applications of the above reactions and the influence of various factors on the yield and direction of the process are examined and the pathways via which they occur are discussed in these reviews.

(b) Dimerisation of other C–H acids. It has been found[240] that, in the presence of copper(I) salts in pyridine, phenyl-substituted acetonitriles are converted by atmospheric oxygen or various peroxide compounds into adiponitrile derivatives[240]. Ketonitriles behave similarly[241,242]. Studies on the oxidative coupling of other C–H acids (arenes, aryl halides, thiophen and its derivatives, etc.) via organocopper compounds with formation of a carbon–carbon bond have been widely developed and have been the subject of a special discussion[13,14].

The catalytic properties of copper salts have been used successfully by a number of investigators for the oxidative polymerisation of aromatic hydrocarbons[243,246]. Copper salts can be used for the oxidative dehydrodimerisation of hydrogen cyanide[247]:

$$N\equiv CH \rightarrow N\equiv C-C\equiv N .$$

It is remarkable that copper(I) and copper(II) oxides as well as various copper(II) salts catalyse the dimerisation–addition of α,β-unsaturated carbonyl compounds—nitriles, esters, and ketones[248-252]:

$$R'CH=CHR \xrightarrow{} R'CH=C(R)C(R')HCH_2R$$
$$R'CH=CHR \xrightarrow{R'=H} RCH_2CH=CHCH_2R$$
$$R'CH=CHR \xrightarrow{CH_2=CHR} R'CH=C(R)CH_2CH_2R ;$$

R = COAlk, COOAlk or CN .

The above reaction is regarded[248-252] as a special type of the Michael addition. A good example of the dehydrocondensation is also the dimerisation of acrylonitrile in the presence of copper(II) ions, which leads to the nitrile of hexenedicarboxylic acid[253]:

$$2CH_2=CHCN \rightarrow NCCH_2CH=CHCH_2CN .$$

(c) Dimerisation of organometallic compounds. The cuprocatalytic dimerisation reactions of Grignard reagents with alkyl halides, which made it possible not only to increase the rate of coupling of the alkyl residues of the above class of compounds but also to apply the method successfully to other syntheses, proved to be particularly productive. Studies in this field have been surveyed by Tamura and Kochi[254]. Analogous question have been partly dealt with in the reviews of Schlosser[255], Posner[11,12], and Normant[8], who considered the problems of the formation of a C–C bond with the aid of organometallic reagents. Another important method of synthesis of various hydrocarbons is the coupling reaction of alkyl, alkenyl, and alkynyl derivatives of lithium, magnesium, zinc, and aluminium, as well as other organometallic compounds in the presence of copper salts[11-14,17,254-257].

2. The Straus–Neuland Dimerisation of Acetylenes

Straus showed that the copper derivative of phenylacetylene dimerises to 1,4-diphenylbut-3-ene-1-yne on heating with acetic acid[258]:

$$C_6H_5C\equiv CCu \rightarrow C_6H_5C\equiv CCH=CHC_6H_5 .$$

Subsequently other workers extended the above reaction to various terminal acetylenes[259-261]. However, the most important result of these studies was the finding that an acid medium promotes the dimerisation of acetylenes, as a result of which cuprocatalytic methods were successfully applied to the dimerisation of acetylene and its monosubstituted homologues to vinylacetylene and its derivatives[2,3,4,80,81,262]:

$$2RC\equiv CH \rightarrow RCH=CHC\equiv CR .$$

The process is usually carried out in a hydrochloric acid solution of copper(I) chloride and is still used in the manufacture of chloroprene from acetylene[80,81,263].

3. Reductive Dehalogenodimerisation Reactions

(a) The Ullmann dehalogenodimerisation of aryl halides. The Ullmann reaction, which consists in the reaction of aryl halides with powdered copper at a high temperature, has

already been widely used for the synthesis of a wide variety of aromatic systems in the course of several decades[264,265]:

$$Ar{-}X \xrightarrow{Cu} Ar{-}Ar + CuX_2 \ .$$

The available literature data on this reaction have been frequently described in reviews[264,265], in which the present limits of the applicability of the reaction, its conditions, and the influence of various substituents and the solvent, as well as the question of the application of a series of copper compounds [copper(I) oxide and copper(I) and copper(II) salts] as additives or independent catalysts are clearly defined; the kinetics of the reaction have been examined in detail and its probable mechanisms have been put forward.

It is appropriate to mention that metallic copper or copper salts in various oxidation states are used successfully also in the so called Ullmann condensation, i.e. in the reaction of aryl halides with anilines[265]:

$$ArCl \xrightarrow{Ar'\text{-}NH_2} ArNHAr' \ .$$

In their studies of the influence of various added copper(I) and copper(II) salts on the Ullmann condensation, some workers[266,267] concluded that copper(I) ions are the catalytically active form for this reaction and that the application of bivalent copper must be accompanied by reducing agents[268].

(b) The dehalogenodimerisation of α-halogenoethers and allyl, propargyl, and benzyl halides. There has been a recent growth of interest in the so-called dehalogenodimerisation reactions of organic halogeno-compounds, which occur in the presence of zerovalent or univalent copper. One of the first reports on this field[269] showed that, on refluxing with metallic copper, various α-chloroethers are converted into ethylene glycol derivatives in high yields:

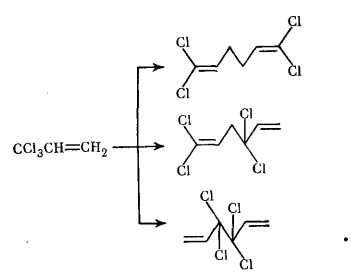
$$RCOCH_2Cl \rightarrow ROCH_2CH_2OR$$
$$R = CH_3,\ ClCH_2CH_2 - \text{ etc.}$$

A little later data were published on the dehalogenodimerisation of allyl halides. Thus Yagupol'skii and Chaika[270] showed that trichloromethylalkenes give rise to chloro-substituted bisallyls and trienes in pyridine in the presence of copper via the mechanism

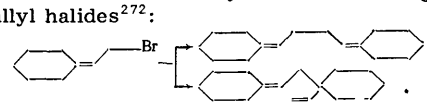
$$RCH{=}CHCCl_3 \rightarrow RCH{=}CHCCl_2CCl_2CH{=}CHR \rightarrow RCH{=}CHCCl{=}CClCH{=}CHR$$
$$R = H,\ C_6H_5,\ COOH,\ COOCH_3 \text{ or } COC_6H_5 \ .$$

It was established that the yield of trienes greatly increases when the reaction is carried out in acetonitrile.

In a somewhat later study it was reported that, in the presence of copper powder in pyridine, trichloromethylethylene dehalogenodimerises to a mixture of all the expected hexadienes[271].



It is of interest that the organocopper complexes obtained from alkyl-lithium and copper iodide in the presence of dialkylamines are effective catalysts of the dehalogenodimerisation of allyl halides[272]:



The results showed that the dehalogenodimerisation reaction is specific only to compounds containing a mobile halogen atom. A study by Japanese workers on the dehalogenodimerisation of allyl and benzyl halides[273,274] provides a good illustration of this postulate. It was observed that both allyl and benzyl chlorides give rise to high yields of dimers in the presence of the copper(I) cation in ethylenediamine, diethylenetetramine, triethylenetetramine, acetylacetone, and ethylenediaminetetra-acetic acid (EDTA):

$$\overset{I}{CuCl} + n\,(en) \rightarrow \overset{I}{Cu}\,(en)_nCl \ ;$$
$$RCH_2Cl + 2\overset{I}{Cu}\,(en)_nCl \rightarrow RCH_2CH_2R + 2\overset{II}{Cu}\,(en)_nCl_2 \ .$$

The replacement of the above solvents by ethanolamine, pyridine, bipyridyl, phenanthroline, or triphenylphosphine suppresses the reaction.

In the presence of the above catalysts [$Cu^I(en)_nCl$] benzyl chloride derivatives (trichloromethylbenzyl, dichlorodiphenylmethane, and chlorodiphenylmethane) behave similarly, with the sole difference that the resulting chloroethanes are then converted into stilbenes[275,276]:

$$C_6H_5C(R)Cl_2 \rightarrow C_6H_5\overset{R}{\underset{|}{C}}Cl{-}\overset{R}{\underset{|}{C}}ClC_6H_5 \rightarrow C_6H_5\overset{R}{\underset{|}{C}}{=}\overset{R}{\underset{|}{C}}C_6H_5 \ ;$$
$$(C_6H_5)_2C(R)Cl \rightarrow (C_6H_5)_2\overset{R}{\underset{|}{C}}{-}\overset{R}{\underset{|}{C}}(C_6H_5)_2 \xrightarrow{R=Cl} (C_6H_5)_2C{=}C(C_6H_5)_2 \ .$$

We may note that this reaction is also catalysed by iron(II) salts.

The available literature data show that the dehalogenation of halogenoalkanes in the presence of both copper salts[276] and zerovalent copper[278-284] is accompanied by partial dehalogenodimerisation with formation of halogenoalkene derivatives.

We believe that, among all the existing ideas concerning the mechanism of the dehalogenodimerisation of allyl systems[271,274], the most likely is the view of Hashimoto and coworkers[274], according to which all these reactions can be interpreted as oxidation-reduction processes via the mechanisms:

$$\overset{I}{Cu} + n\,(en) \rightarrow \overset{I}{Cu}\,(en)_n \ ;$$
$$RCH_2Cl \xrightarrow{\overset{I}{Cu(en)_n}} RCH_2CH_2R + \overset{II}{CuCl_2} \ ,$$

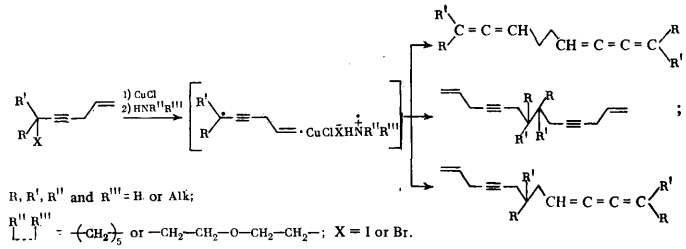
or

$$2RCH_2Cl \xrightarrow{\overset{I}{CuCl}} 2\,[RCH_2Cl \ldots CuCl \leftrightarrow R\dot{C}H_2\overset{II}{Cl}CuCl] \rightarrow RCH_2CH_2R + \overset{II}{CuCl_2} \ ,$$

or

$$RCH_2Cl \xrightarrow{\overset{I}{CuCl}} RCH_2ClCuCl \xrightarrow{\overset{I}{CuCl}} RCH_2\overset{I}{C}uCl + CuCl_2 \ ;$$
$$2RCH_2\overset{I}{C}uCl \rightarrow RCH_2CH_2R + 2\overset{I}{RC}uCl \ .$$

Badanyan showed recently that vinylpropargyl halides are converted into a mixture of unsaturated hydrocarbons in the presence of copper(I) salts and amines (primary or secondary) via dehalogenodimerisation[285-295]. The authors believe that the process proceeds via the mechanism



R, R', R'' and R''' = H or Alk;

R'' R''' = $-(CH_2)_5-$ or $-CH_2-CH_2-O-CH_2-CH_2-$; X = I or Br.

It was shown that complexes of copper salts with amines containing hydrogen attached to the nitrogen atom exhibit a catalytic activity, the yield of product depending greatly on the ionisation potential of the amines[288,293,295].

The study of the influence of substituents in various positions in the system revealed certain regularities. Thus it has been found that an increase in the bulk of the alkyl groups at the carbon atom attached to the halogen in vinylpropargyl halides not only decreases the overall yield of hydrocarbons but also increases the fraction of anomalous dehalogenodimerisation products—unsaturated hydrocarbons with cumulated multiple bonds[286,288,295].

An interesting picture was observed when vinylpropargyl halides with substituents at the double bond were introduced into the reaction. Thus in the case of vicinal substitution (at the double bond) of the halides, the yield of the anomalous dehalogenodimerisation products increases; in contrast, geminally substituted or trisubstituted unsaturated halides give rise only to dienediyne hydrocarbons[290,291]:

$$RR'C(X)C{\equiv}CC(CH_3){=}CHR'' \rightarrow HC(R'){=}C(CH_3)C{\equiv}CC(RR')C(RR')C{\equiv}CC(CH_3){=}CHR'';$$

R, R′, and R″ = H or alkyl.

The different types of behaviour of the systems investigated can be readily accounted for within the framework of the electronic effects of the substituents and the steric hindrance generated by them. In the study of the effect of the medium and also of various additives on this reaction, it was concluded[293,295] that the reaction proceeds via the formation of radical intermediates. Here it is important that, when a reducing agent (hydroxylamine hydrochloride), is introduced into the reaction medium, the reaction becomes catalytic[295].

It is noteworthy that, under the conditions of the dehalogenodimerisation of vinylpropargyl halides, allyl chlorides containing electron-accepting substituents also enter into this reaction[292]:

$$RR'C{=}C(R'')CH_2Cl \rightarrow RR'C{=}C(R'')CH_2CH_2C(R''){=}CRR'';$$
R, R′ and R″ = H or Cl.

There are literature data concerning the reductive dimerisation of ethers of acetylenic carbinols[296], allenic halides[297], and other systems[298] catalysed by copper or its salts.

It has been reported that in the presence of metallic copper trichloromethylbenzene dehalogenodimerises to dichlorostilbene[299]:

$$C_6H_5CCl_3 \rightarrow C_6H_5CCl{=}CClC_6H_5.$$

The dehalogenodimerisation of α-halogenoacids[300]

$$RR'CBrCOOR'' \rightarrow RR'C(COOR'')\text{–}CRR'(COOR'')$$

and of acid chlorides[301]

$$RCOCl \rightarrow RCOCOR$$

is of interest from the practical point of view.

Finally one should note that the amine complexes of copper(I) salts catalyse the intramolecular cyclisation of propargyl ethers[302].

---o0o---

It is evident from the above that during recent years definite advances have been made in the field of cuprocatalytic reactions on the basis of which methods of synthesis of many types of organic compounds have been developed. These processes are undoubtedly still of enormous interest, as shown by the vigorous present development of homogeneous cuprocatalysis based on isonitrile complexes of copper and its salts. The above catalysts are used widely for the synthesis of derivatives of cyclopropane, cyclobutane, cyclopentane, oxazoline, oxazine, imidazoline, thiazole, pyrroline, etc. Earlier data on this field have been surveyed[303]. Synthetic studies on these lines are being continued[304–312]. It is remarkable that copper complexes of the above type catalyse the insertion of isonitriles in the heteroatom—hydrogen bond in amines[311,313,314], alcohols[308,315,316], thiols[317,318], phosphines[319], and silanes[330] and also the esterification of alkanoic, halogenoalkanoic, and halogenoarenoic acids and their anhydrides[321–323]. Isonitrile complexes of copper are used in the binding of carbon dioxide[324–329] and in prototropic[314] and *cis–trans*[323,330] isomerisations. It is extremely important that they catalyse the Michael, Tishchenko, Meerwein–Ponndorf, and analogous reactions[251,330–338], the dimerisation of α,β-unsaturated nitriles and carbonyl compounds[248,249,330–332,339], and the polymerisation of alkenes and their derivatives[340–343]. There is no doubt about the prospects for the further development of both the theoretical and practical aspects of cuprocatalytic reactions; a more profound understanding of their essential features and their control are the tasks for the immediate future.

REFERENCES

1. L.P.Yur'eva, Uspekhi Khim., 1974, **43**, 95 [Russ. Chem.Rev., 1974(1)].
2. A.Miyashite and A.Yamamoto, Bull.Chem.Soc.Japan, 1977, **50**, 1102.
3. O.N.Temkin and R.A.Flid, "Kataliticheskoe Prevrashchenie Atsetilenovykh Soedinenii v Rastvorakh Kompleksov Metallov" (Catalytic Reactions of Acetylenic Compounds in Solutions of Metal Complexes), Izd.Nauka, Moscow, 1968, p.69.
4. R.G.R.Bacon and H.A.O.Hill, Quart.Rev., 1964, **19**, 95.
5. A.M.Sladkov and L.Yu.Ukhin, Uspekhi Khim., 1968, **37**, 1747 [Russ.Chem.Rev., 1968(10)].
6. A.M.Sladkov and I.R.Gol'ding, Uspekhi Khim., 1979, **48**, 1625 [Russ.Chem.Rev., 1979(9)].
7. M.Goshaev, O.S,Otroshchenko, and A.S.Sadykov, Uspekhi Khim., 1972, **41**, 1928 [Russ.Chem.Rev., 1972(10)].
8. J.F.Normant, Synthesis, 1972, 63.
9. J.F.Normant, Pure Appl.Chem., 1978, **50**, 709.
10. A.N.Nesmeyanov and K.A.Kochetkov, "Metody Elementoorganicheskoi Khimii" (Methods of Organoelemental Chemistry), Izd.Nauka, Moscow, 1974, p.11.
11. G.H.Posner, Org.Reactions, 1972, **19**, 1.
12. G.H.Posner, Org.Reactions, 1975, **22**, 253.
13. T.Kauffman, Angew.Chem., Int.Ed., 1974, **13**, 291.
14. T.Kauffman, Angew.Chem., 1974, **86**, 321.
15. J.E.Gowan and T.S.Wheeler, "Name Index of Organic Reactions", Longmans, Great Britain, 1960, pp.5, 100.
16. M.G.Jaquemin, Bull.Soc.chim.France, 1885, **43**, 556.
17. A.E.Jukes, Adv.Organometal.Chem., 1974, **12**, 215.
18. F.Straus, Annalen, 1905, **342**, 201.
19. G.M.Whitesides and C.P.Casey, J.Amer.Chem.Soc., 1966, **88**, 4541.
20. G.M.Whitesides, C.P.Casey, and J.K.Kriger, J.Amer. Chem.Soc., 1971, **93**, 1379.
21. T.Kauffman and W.Sahm, Angew.Chem., 1967, **79**, 101.
22. T.Kauffman and W.Sahm, Angew.Chem., Int.Ed., 1967, **6**, 85.
23. G.M.Whitesides, J.SanFillipo, C.P.Casey, and E.J.Panek, J.Amer.Chem.Soc., 1967, **89**, 5302.

24. C.F.Castro, E.J.Gaughan, and D.C.Owsley, J.Org. Chem., 1966, **31**, 4071.
25. M.Nilsson, Tetrahedron Letters, 1966, 679.
26. E.J.Corey and G.H.Posner, J.Amer.Chem.Soc., 1967, **89**, 3911.
27. H.O.House, W.H.Respess, and G.M.Whitesides, J.Org. Chem., 1966, **31**, 3128.
28. E.J.Corey and J.A.Katzenellenbogen, J.Amer.Chem. Soc., 1969, **91**, 1851.
29. L.A.Yanovskaya, Uspekhi Khim., 1967, **36**, 965 [Russ. Chem.Rev., 1967(6)].
30. F.A.Cotton, Chem.Rev., 1955, **55**, 551.
31. G.W.Parshel and J.J.Mrowca, Adv.Organometal.Chem., 1968, **7**, 157.
32. C.D.M.Bevervijk and G.J.M.Van der Kerk, Organometal.Chem.Rev., 1970, **A5**, 215.
33. T.A.Turney, "Oxidation Mechanisms" (Translated into Russian), Izd.Mir, Moscow, 1968, p.127.
34. H.O.House, Acc.Chem.Res., 1976, **9**, 59.
35. F.Miniski, Acc.Chem.Res., 1975, **8**, 165.
36. J.K.Kochi, Acc.Chem.Res., 1974, **7**, 351.
37. J.A.Neuland and W.Z.Fooly, Proc.Ind.Acad.Sci., 1929, **38**, 196; Chem.Abs., 1931, **25**, 2683.
38. A.L.Klebanskii, A.S.Vol'kenshtein, and A.P.Orlova, Zhur.Obshch.Khim., 1935, **5**, 1254.
39. K.Shimo, J.Chem.Soc.Japan, 1942, **63**, 315; Chem. Abs., 1947, **41**, 3038.
40. E.Adler, Swedish P.123 613 (1948); Chem.Abs., 1949, **43**, 6218,
41. US P.2 809 221 (1957).
42. BRD P.968 921 (1958).
43. BRD P.1 011 414 (1957).
44. BRD P.1 094 102 (1958).
45. BRD P.1 094 734 (1960); Chem.Abs., 1961, **55**, 25 754.
46. BRD P.1 097 977 (1961).
47. B.P.736 375 (1955); Chem.Abs., 1956, **50**, 8705.
48. B.P.787 904 (1957); Chem.Abs., 1958, **52**, 10 141.
49. French P.1 383 381 (1964); Chem.Abs., 1965, **62**, 9008.
50. R.Olson, Acta Chem.Scand., 1966, **20**, 585.
51. Swedish P.6 510 390 (1966); Chem.Abs., 1966, **65**, 3744.
52. US P.6 611 776 (1967); Chem.Abs., 1967, **67**, 63 726.
53. A.E.Kalaidzhyan, K.A.Kurginyan, and G.A.Chukhadzhyan, USSR P.374 290 (1971); Byul.Izobret., 1975, No.15, 47.
54. K.A.Kurginyan, R.G.Karapetyan, and G.A.Chukhadzhyan, Arm.Khim.Zhur., 1974, **27**, 661.
55. G.M.Mkryan, N.A.Papazyan, and G.A.Chukhadzhyan, Arm.Khim.Zhur., 1966, **19**, 192.
56. K.A.Kurginyan, R.G.Karapetyan, and G.A.Chukhadzhyan, Arm.Khim.Zhur., 1972, **25**, 270.
57. G.E.Castro, E.J.Gaughan, D.C.Owsley, J.Org.Chem., 1965, **30**, 587.
58. V.H.Kleinnetand and H.Fürst, J.prakt.Chem., 1967, **36**, 252.
59. G.M.Mkryan, D.G.Rafaelyan, E.S.Voskanyan, and N.A.Papazyan, Arm.Khim.Zhur., 1972, **25**, 309.
60. G.M.Mkryan, D.G.Rafaelyan, L.K.Arushanyan, and N.A.Papazyan, Arm.Khim.Zhur., 1972, **25**, 129.
61. R.G.Karaptyan, Candidate's Thesis in Chemical Sciences, Erevan State University, Erevan, 1977.
62. G.M.Mkryan, D.G.Rafaelyan, and N.A.Papazyan, Arm. Khim.Zhur., 1974, **27**, 748.
63. D.G.Rafaelyan, N.A.Papazyan, A.P.Adamyan, and G.M.Mkryan, Arm.Khim.Zhur., 1975, **28**, 585.
64. D.V.Sokol'skii, Ya.A.Dorfman, Z.F.Prazdnikova, and I.V.Rodnikova, Zhur.Org.Khim., 1973, **9**, 1569.
65. O.N.Temkin and R.M.Flid, "Problemy Kinetiki i Kataliza" (Problems of Kinetics and Catalysis), Izd. Nauka, Moscow, 1968, p.98.
66. S.M.Brailovskii, E.A.Baiko, O.N.Temkin, A.S.Kostyushin, and R.M.Flid, Kinetika i Kataliz, 1973, **14**, 513.
67. D.V.Sokol'skii, Ya.A.Dorfman, and Z.F.Prazdnikova, Zhur.Org.Khim., 1971, **7**, 2048.
68. L.G.Bruk, S.M.Brailovskii, O.N.Temkin, and R.M.Flid, Kinetika i Kataliz, 1974, **15**, 516.
69. S.M.Brailovskii, M.G.Bruk, A.S.Kostyushin, O.N.Temkin, and R.M.Flid, Kinetika i Kataliz, 1973, **14**, 1222.
70. K.A.Kurginyan, Arm.Khim.Zhur., 1968, **21**, 128.
71. Japanese P.6 804 850 (1967); Chem.Abs., 1969, **69**, 105 868.
72. T.Kunugi, H.Tominago, and T.Nishimura, Kogyo Kagaku Zasshi, 1970, **73**(1), 170; Chem.Abs., 1970, **72**, 131 938.
73. S.V.Al'tshuler, R.M.Flid, and A.A.Englin, Neftekhimiya, 1971, **10**, 259.
74. R.P.Argenbright, J.Org.Chem., 1962, **27**, 1205.
75. US P.3 406 215 (1969).
76. W.C.Baird and J.H.Surridge, J.Org.Chem., 1970, **35**, 2090.
77. W.C.Baird, J.H.Surridge, and M.Buza, J.Org.Chem., 1971, **36**, 2088.
78. W.C.Baird, J.H.Surridge, and M.Buza, J.Org.Chem., 1971, **36**, 3324.
79. S.Uemura, A.Tabata, Y.Kimura, and K.Tchikawa, Bull.Chem.Soc.Japan, 1971, **44**, 1973.
80. J.A.Neuland and R.Vogt, "The Chemistry of Acetylene" (Translated into Russian), Inostr.Lit., Moscow, 1947, p.157.
81. S.A.Vartanyan, "Khimiya Vinilatsetilena i Ego Proizvodnykh" (The Chemistry of Vinylacetylene and Its Derivatives), Izd.Akad.Nauk Arm.SSR, Erevan, 1966, p.86.
82. A.A.Petrov, Uspekhi Khim., 1960, **29**, 1049 [Russ. Chem.Rev., 1960(9)].
83. R.G.Agababyan, Candidate's Thesis in Chemical Sciences, Erevan State University, Erevan, 1975.
84. US P.2 322 696 (1944); Chem.Abs., 1944, **38**, 118.
85. M.Asscher and D.Vofsi, Chem.Ind.(London), 1962, 209.
86. M.Asscher and D.Vofsi, J.Chem.Soc., 1963, 1887.
87. M.Asscher and D.Vofsi, J.Chem.Soc., 1963, 3921.
88. M.Asscher and D.Vofsi, J.Chem.Soc., 1964, 4962.
89. M.Asscher, Chem.Ind.(London), 1964, 32.
90. S.Murai and S.Tsutsumi, J.Org.Chem., 1965, **31**, 3000.
91. D.J.Burton and L.J.Kehoe, J.Org.Chem., 1970, **35**, 1339.
92. D.J.Burton and L.J.Kehoe, J.Org.Chem., 1971, **36**, 2596.
93. I.B.Afanas'ev and G.I.Samokhvalov, Uspekhi Khim., 1969, **38**, 687 [Russ.Chem.Rev., 1969(4)].
94. Sh.O.Badanyan, A.N.Stepanyan, and K.L.Sarkisyan, Arm.Khim.Zhur., 1974, **27**, 479.
95. Sh.O.Badanyan, A.N.Stepanyan, and A.A.Gevorkyan, Arm.Khim.Zhur., 1971, **24**, 498.
96. Sh.O.Badanyan, A.N.Stepanyan, and A.A.Gevorkyan, Arm.Khim.Zhur., 1972, **25**, 820.
97. Sh.O.Badanyan, K.L.Sarkisyan, and A.A.Gevorkyan, Arm.Khim.Zhur., 1971, **24**, 589.
98. A.A.Gevorkyan, Sh.O.Badanyan, and A.N.Stepanyan, Arm.Khim.Zhur., 1974, **27**, 802.
99. Sh.O.Badanyan and A.N.Stepanyan, Arm.Khim.Zhur., 1974, **27**, 288.
100. Belgian P.654 544 (1966); Chem.Abs., 1966, **65**, 5404.

101. French P.1 409 516 (1966); Chem.Abs., 1966, **64**, 3364.
102. W.F.Truce, C.T.Goralski, L.W.Christemsen, and R.H.Bavry, J.Org.Chem., 1970, **35**, 4217.
103. W.F.Truce and C.T.Goralski, J.Org.Chem., 1970, **35**, 4220.
104. M.D.Stadnichuk, T.B.Kryukova, and A.A.Petrov, Zhur.Obshch.Khim., 1975, **45**, 839.
105. M.M.Taneskov and M.D.Stadnichuk, Zhur.Obshch. Khim., 1975, **45**, 843.
106. T.B.Kryukova, M.D.Stadnichuk, and A.A.Petrov, Zhur.Obshch.Khim., 1973, **43**, 1063.
107. T.B.Kryukova, M.D.Stadnichuk, and T.N.Timofeeva, Zhur.Obshch.Khim., 1974, **44**, 789.
108. A.V.Dombrovskii, Uspekhi Khim., 1957, **26**, 689.
109. C.S.Rondestvedt, "Organic Reactions" (Translated into Russian), 1965, Vol.11, p.199.
110. A.A.Matnishyan, Doctoral Thesis in Chemical Sciences, Institute of General Chemistry of the Academy of Sciences, of Armenian SSR, Erevan, 1977.
111. S.Patai, "The Chemistry of Alkenes" (Translated into Russian), Izd.Khimiya, Leningrad, 1969, p.374.
112. V.O.Babayan, Doctoral Thesis in Chemical Sciences, Erevan State University, Erevan, 1971.
113. N.I.Ganushchak, Doctoral Thesis in Chemical Sciences, Lensovet Leningrad Technological Institute, Leningrad, 1973.
114. H.G.Viehe, "Chemistry of Acetylenes" (Translated into Russian), Izd.Khimiya, Moscow, 1973, p.224.
115. W.Reppe, Annalen, 1955, **596**, 25.
116. BRD P.871 005 (1953); Chem.Abs., 1956, **50**, 8713.
117. B.P.676 601 (1952); Chem.Abs., 1953, **47**, 7533.
118. S.Murahashi, J.Chem.Soc.Japan, Ind.Chem.Sect., 1953, **56**, 17; Chem.Abs., 1954, **48**, 7536.
119. S.Murahashi, Chem.Eng.Japan, 1952, **16**, 35; Chem. Abs., 1952, **46**, 2858.
120. R.Suzuki, Rev.Phys.Chem.Japan, 1953, **23**, 57, 66.
121. US P.2 487 006 (1949); Chem.Abs., 1950, **44**, 5380.
122. R.Paul and S.Tchelitcheff, Bull.Soc.chim.France, 1953, 417.
123. BRD P.890 956 (1953); Chem.Zentr., 1954, **125**, 4720.
124. I.M.Heilbron, and E.R.H.Jones, J.Chem.Soc., 1947, 1589.
125. P.G.Sergeev, V.I.Lyubolob, and A.N.Bogatyreva, Khim.Nauka i Prom., 1957, **2**, 272.
126. G.A.Chukhadzhyan, R.A.Melikyan, Sh.A.Babayan, and S.A.Vartanyan, Izv.Akad.Nauk Arm.SSR, 1961, **14**, 445.
127. A.N.Shapovalova, Zhur.Prikl.Khim., 1963, **36**, 904.
128. G.N.Freidlina and L.A.Golubko, Zhur.Prikl.Khim., 1964, **37**, 176.
129. A.M.Murenkov, G.N.Freidlina, and N.I.Rodchenko, USSR P.191 491 (1966); Byul.Izobret., 1967, No.4, 21.
130. A.M.Murenkov and G.N.Freidlina, Khim.Prom., 1968, **44**, 885.
131. Yung-Yao Chen, Yuen-Chen Chin, and Hua Hsuch Tung Pao, 1958, No.11, 658; Chem.Abs., 1962, **56**, 306.
132. US P.3 108 140 (1963).
133. I.M.Heilbron, E.R.H.Jones, and F.Sondheimer, J.Chem.Soc., 1947, 1586.
134. M.Iwata and S.Emoto, Bull.Chem.Soc.Japan, 1974, **47**, 2907.
135. M.Iwata and S.Emoto, Bull.Chem.Soc.Japan, 1976, **49**, 1369.
136. G.G.Rozantsev, A.A.Fainzil'berg, and S.S.Novikov, Usepkhi Khim., 1965, **34**, 177 [Russ.Chem.Rev., 1965(2)].
137. E.Chinopers, Chem.Rev., 1963, **63**, 235.
138. C.Köbrich, Angew.Chem., 1972, **84**, 557.
139. R.Borler and Vo.-Quang, Bull.Chem.Soc.chim.France, 1969, 3729.
140. W.Kirmse, "Carbene Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1966, p.120.
141. L.F.Hatch and R.R.Estes, J.Amer.Chem.Soc., 1945, **67**, 1730.
142. L.F.Hatch and G.B.Roberts, J.Amer.Chem.Soc., 1946, **68**, 1196.
143. L.F.Hatch, A.N.Brown, and H.P.Bailey, J.Amer. Chem.Soc., 1950, **72**, 3198.
144. L.F.Hatch, L.O.Morgan, and V.L.Tveedie, J.Amer. Chem.Soc., 1952, **74**, 1826.
145. Yu.A.Treger, R.M.Flid, and N.A.Vorontsova, Kinetika i Kataliz, 1966, **7**, 449.
146. R.E.Kepper and L.J.Andrews, J.Org.Chem.Soc., 1948, **13**, 208.
147. L.J.Andrews and R.M.Keefer, J.Amer.Chem.Soc., 1948, **70**, 3261.
148. J.Jacques, Bull.Soc.chim.France, 1945, 843.
149. A.G.Muradyan, N.M.Morlyan, S.M.Gabrielyan, and Sh.O.Badanyan, Zhur.Org.Khim., 1974, **10**, 1122.
150. N.M.Morlyan, A.G.Muradyan, and Sh.O.Badanyan, Arm.Khim.Zhur., 1975, **28**, 633.
151. A.G.Muradyan, S.M.Gabrielyan, N.M.Morlyan, M.K.Mardoyan, and Sh.O.Badanyan, Prom.Aremenii, 1973, **11**, 21.
152. G.F.Hager, US P.2 462 388 (1949); Chem.Abs., 1949, **43**, 4286.
153. G.C.Bassler, US P.2 646 443 (1953); Chem.Abs., 1954, **48**, 7048.
154. J.K.Johnson and G.M.Witman, US P.2 477 617 (1949); Chem.Abs., 1950, **44**, 4023.
155. N.M.Morlyan, A.G.Muradyan, L.O.Esayan, and Sh.O.Badanyan, Arm.Khim.Zhur., 1975, **28**, 75.
156. BRD P.801 330 (1951); Chem.Abs., 1951, **45**, 3408.
157. J.R.L.Smith and Z.A.Malik, J.Chem.Soc., 1970B, 920.
158. N.N.Vorozhtsov and V.A.Kobelov, Dokl.Akad.Nauk SSSR, 1934, **3**, 108.
159. US P.1 994 845 (1935); Chem.Abs., 1935, **29**, 2973.
160. N.N.Vorozhtsov and V.A.Kobelov, Zhur.Obshch. Khim., 1934, **4**, 310.
161. F.Linsner and R.L.Evans, J.Org.Chem., 1945, **10**, 283.
162. US P.2 455 931 (1948); Chem.Abs., 1949, **43**, 3454.
163. B.P.839 420 (1960); Chem.Abs., 1960, **54**, 24 549.
164. B.A.Krentsel', A.V.Topchiev, and D.E.Il'ina, Dokl. Akad.Nauk SSSR, 1956, **110**, 994.
165. US P.3 449 450 (1969).
166. A.Lorenzini and C.Walling, J.Org.Chem., 1967, **32**, 4008.
167. J.K.Kochi, J.Amer.Chem.Soc., 1955, **77**, 5274.
168. K.B.Doifode, J.Org.Chem., 1962, **27**, 2665.
169. E.R.Glazier, J.Org.Chem., 1962, **27**, 2937.
170. P.B.Sollman and R.M.Dodson, J.Org.Chem., 1961, 26, 4180.
171. J.Y.Samon and K.Nishzawa, Chem.Comm., 1973, 83.
172. Y.Kojima, K.Usui, and S.Kawaguchi, Bull.Soc.Chem. Japan, 1972, **45**, 3125.
173. Y.Kojima and S.Kawaguchi, Bull.Soc.Chem.Japan, 1972, **45**, 1293.
174. K.M.Smirnov, A.P.Tomilova, and A.I.Shchekotikhin, Uspekhi Khim., 1967, **36**, 777 [Russ.Chem.Rev., 1967(5)].
175. R.Kouw, Synthetic Comm., 1971, **1**, 125.
176. L.B.Fisher, Uspekhi Khim., 1958, **27**, 589.
177. I.A.Chekulaeva and L.V.Kondrateva, Uspekhi Khim., 1965, **34**, 1583 [Russ.Chem.Rev., 1965(9)].

178. B.I.Belov and V.V.Kozlov, Uspekhi Khim., 1963, **32**, 121 [Russ.Chem.Rev., 1963(2)].
179. K.Kochi, J.Amer.Chem.Soc., 1957, **79**, 2942.
180. B.P.775 723 (1957); Chem.Abs., 1957, **51**, 16 511.
181. BRD P.1 048 909 (1959); Chem.Abs., 1961, **55**, 2480.
182. J.Colonge and R.Falcotet, Bull.Soc.chim.France, 1957, 1166.
183. J.Colonge and R.Falcotet, Compt.rend., 1956, **242**, 1484.
184. L.Brandsma, "Preparative Acetylenic Chemistry", Elsevier Publ., New York, 1971, p.30.
185. P.Korts, Annalen, 1962, **685**, 6.
186. A.M.Sladkov, L.Yu.Ukhin, and V.V.Korshak, Izv. Akad.Nauk SSSR, Otd.Khim.Nauk, 1963, **111**, 2213.
187. J.Colonge and M.A.Varagnet, Bull.Soc.chim.France, 1964, 561.
188. F.S.Kinoyan, S.K.Pirenyan, and S.A.Vartanyan, Arm. Khim.Zhur., 1971, **24**, 871.
189. A.Sevin, W.Chodkievicz, and P.Cadiot, Tetrahedron Letters, 1965, 1953.
190. A.Sevin, W.Chodkievicz, and P.Cadiot, Bull.Soc.chim. France, 1974, 913.
191. C.S.L.Baker and P.D.Landor, J.Chem.Soc., 1965, 4659.
192. R.V.Stevenes and E.B.Reid, Tetrahedron Letters, 1975, **48**, 4193.
193. T.Saegusa, I.Murase, and Y.Ito, Curr.Abs.of Chem. and Index Chemistry, 1971, **43**, 182 493.
194. A.M.Malte and C.E.Castro, J.Amer.Chem.Soc., 1967, **89**, 6770.
195. R.E.Atkinson, R.F.Curtis, and J.A.Taylor, J.Chem. Soc.C, 1967, 578.
196. C.E.Castro and R.D.Stephens, J.Org.Chem., 1963, **28**, 2163.
197. R.D.Stephens and C.E.Castro, J.Org.Chem., 1963, **28**, 3313.
198. J.F.Normant, M.Bourgain, and A.M.Rone, Compt.rend., 1970, **C270**, 354.
199. C.E.Castro, R.Havlin, V.K.Honwad, A.Malte, and S.Moje, J.Amer.Chem.Soc., 1969, **91**, 6464.
200. K.Gump, S.Moje, and S.E.Castro, J.Amer.Chem.Soc., 1967, **89**, 6770.
201. J.Burdon, P.L.Coe, C.R.Marsh, and J.C.Tatlow, Chem.Comm., 1967, 1259.
202. G.Van Koten, W.M.Richard, T.Hoedt, and J.G.Noltes, J.Org.Chem., 1977, **42**, 2705.
203. M.Bourgain and J.F.Normant, Bull.Soc.chim.France, 1973, 2137.
204. J.A.Otto, US P.2 422 252 (1947); Chem.Abs., 1947, **41**, 6273.
205. B.P.569 719 (1945); Chem.Abs., 1947, **41**, 6273.
206. G.W.Herne and D.C.France, US P.2 446 475 (1948); Chem.Abs., 1949, **43**, 663.
207. US P.2 911 450 (1959).
208. French P. 1 326 286 (1963); Chem.Abs., 1963, **59**, 11 246.
209. B.P.1 300 430 (1972).
210. B.P.1 306 548 (1973).
211. W.Strohmeier, Z.Naturforsch., 1974, **29**, 282.
212. P.Chang and Hua Hsueh Hsuek Pao, Acta Chim.Sinica, 1960, **26**, 117; Ref.Zhur.Khim., 1961, 8B471.
213. US P.3 061 653 (1962); Chem.Abs., 1963, **58**, 5514.
214. T.A.Favorskaya, Zhur.Obshch.Khim., 1939, **9**, 1237.
215. A.N.Pudovik, Zhur.Obshch.Khim., 1951, **21**, 1811.
216. S.A.Vartanyan and Sh.O.Badanyan, Uspekhi Khim., 1967, **36**, 1563 [Russ.Chem.Rev., 1967(9)].
217. J.H.Wotiz, "Propargylic Rearrangements", in H.G.Viehe, "Chemistry of Acetylenes", Marcel Dekker, New York, 1969, p.365.
218. D.R.Taylor, 1967, **67**, 317.
219. M.V.Mavrov and V.F.Kucherov, Usepkhi Khim., 1967, **36**, 553 [Russ.Chem.Rev., 1967(4)].
220. V.F.Kucherov, M.V.Mavrov, and A.R.Derzhinskii, "Prirodnye Poliatsetilenovye Soedineniya" (Natural Polyacetylenic Compounds), Izd.Nauka, Moscow, 1972, p.40.
221. M.Yu.Kogan, R.M.Flid, and N.S.Prostakov, "Trudy Instituta Tonkoi Khimicheskoi Tekhnologii" (Transactions of the Institute of Fine Chemical Engineering), Moscow, 1955, p.45.
222. G.Eadon and S.M.Younus, J.Amer.Chem.Soc., 1974, **96**, 2288.
223. A.N.Nesmeyanov and K.A.Kochetkov, "Metody Elementoorganicheskoi Khimii. Khloralitfaticheskie Soedineniya" (Methods of Organoelemental Chemistry. Aliphatic Chloro-Compounds), Izd.Nauka, Moscow, 1973.
224. B.P.653 347 (1961); Chem.Abs., 1952, **46**, 1583.
225. N.V.Bogdan, T.G.Gun'ko, and L.A.Zaichenko, Vestnik Khar'kov.Polimer.Inst., 1974, **98**, 21.
226. B.Tamamushi, Bull.Chem.Soc.Japan, 1942, **17**, 417; Chem.Abs., 1947, **41**, 4455.
227. P.Yater and J.Fugger, Chem.Ind.(London), 1957, 1511; Chem.Abs., 1958, **52**, 6259.
228. P.G.Gassman and F.S.Williams, Tetrahedron Letters, 1971, 1409.
229. I.Takashi and S.Masaki, Japanese P.48 412 (1974); Ref.Zhur.Khim., 1975, 20N102.
230. J.D.Miller and D.S.Morton, Inorg.Nuclear Chem. Letters, 1975, **11**, 1.
231. C.S.Rondesvedt and G.J.Mantell, J.Amer.Chem.Soc., 1961, **82**, 6419.
232. C.Glaser, Ber., 1869, **2**, 422.
233. E.Eglinton and A.R.Galbraith, Chem.Ind.(London), 1956, 737.
234. W.Chodkiewicz, Ann.Chim., 1957, 819.
235. W.Chodkiewicz, J.S.Alhowalin, P.Cadiot, and A.Wilemort, Compt.rend., 1957, **245**, 322.
236. F.Eglinton and W.McCrae, Adv.Org.Chem., 1963, **4**, 225.
237. F.Eglinton and W.McCrae, "Advances in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1966, Vol.4, p.239.
238. F.Bohlmann, H.Schonowsky, E.Inhoffen, and G.Grau, Ber., 1964, **97**, 794.
239. I.L.Kotlyarevskii, M.S.Shvartsberg, and L.B.Fisher, "Reaktsii Atsetilenovykh Soedinenii" (Reactions of Acetylenic Compounds), Izd.Nauka, Novosibirsk, 1967, p.173.
240. M.S.Kharach and G.Sosnovsky, Tetrahedron, 1958, **97**, 105.
241. H.A.P.Jongh, C.R.H.I.Jonge, and W.J.Mijs, J.Org. Chem., 1971, **36**, 3160.
242. H.A.P.Jongh, C.R.H.I.Jonge, and W.J.Mijs, J.Org. Chem., 1972, **37**, 1960.
243. P.Kovacic and A.Ryriakis, J.Amer.Chem.Soc., 1963, **85**, 454.
244. P.Kovacic and A.Ryriakis, Tetrahedron Letters, 1962, 467; Chem.Abs., 1962, **57**, 13 966.
245. E.Tsuchida, M.Kaneko, and N.Hiroyki, Makromol. Chem., 1972, **151**, 221.
246. E.Tsuchida, N.Hiroyki, and T.Nishiyama, J.Polymer Sci., 1974, No.47, 35.
247. Sagami Chemical Research Centre, B.P.1 084 477; Chem.Abs., 1967, **67**, 110 196.
248. T.Saegusa, Y.Ito, S.Tomita, and H.Konoshita, J.Org.Chem., 1970, **35**, 670.
249. T.Saegusa, Y.Ito, H.Kinoshita, and S.Tomita, Bull. Chem.Soc.Japan, 1970, **43**, 877.

250. US P.3 641 106 (1972).
251. T.Saegusa, Y.Ito, H.Kinoshita, and S.Tomita, Bull. Chem.Soc.Japan, 1972, **45**, 496.
252. Japanese P.40 448 (1974); Ref.Zhur.Khim., 1975, 16N89.
253. C.A.Buehler and D.E.Pearson, "Survey of Organic Syntheses" (Translated into Russian), Izd.Mir, Moscow, 1973, Vol.1, p.135.
254. M.Tamura and J.K.Kochi, J.Organometall.Chem., 1972, **42**, 205.
255. M.Schlosser, Angew.Chem., Int.Ed., 1974, **13**, 701.
256. S.Takeo, I.Tetsuo, and I.Yoshihiko [tentative spelling (Ed.of Translation)], J.Chem.Soc.Japan, Ind.Chem. Sect., 1969, **72**, 1627.
257. G.Zweifel and R.L.Miller, J.Amer.Chem.Soc., 1970, **92**, 6678.
258. F.Straus, Annalen, 1905, **342**, 190.
259. M.Akhtar and B.C.L.Weedon, Proc.Chem.Soc., 1958, 303.
260. M.Akhtar, T.A.Richard, and B.C.L.Weedon, J.Chem. Soc., 1959, 933.
261. L.Sattaböl, Acta Chem.Scand., 1959, **13**, 198.
262. K.A.Kurginyan, Candidate's Thesis in Chemical Sciences, Erevan State University, Erevan, 1969.
263. A.A.Petrov, Uspekhi Khim., 1944, **13**, 203.
264. P.E.Franta, Chem.Rev., 1946, **38**, 139.
265. P.E.Franta, Chem.Rev., 1964, **64**, 613.
266. V.V.Litvak and S.M.Shein, Zhur.Obshch.Khim., 1975, **11**, 903.
267. H.Mitsuhiko, J.Fac.Eng.Univ., 1970, **8**, 58; Ref. Zhur.Khim., 1973, 22B915.
268. T.D.Tuong and H.Mitsuhiko, Chem.Letters, 1973, No.4, 363.
269. K.Teramura and R.Oda, J.Chem.Soc.Japan, Ind.Chem. Sect., 1951, **54**, 605.
270. L.M.Yagupol'skii and E.A.Chaika, Zhur.Org.Khim., 1966, 2, 1744.
271. W.R.Dolbier and G.A.Hopman, Chem.Comm., 1971, 150.
272. Y.Kitagawa, K.Oshima, H.Yamamoto, and H.Nozaki, Tetrahedron Letters, 1975, 1859.
273. T.Kawaki and H.Hashimoto, Bull.Chem.Soc.Japan, 1972, **45**, 3130.
274. K.Wada and H.Hashimoto, Bull.Chem.Soc.Japan, 1968, **41**, 3001.
275. K.Onuma, J.Yamshito, and H.Hashimoto, Bull.Chem. Soc.Japan, 1970, **43**, 837.
276. K.Onuma and H.Hashimoto, Bull.Chem.Soc.Japan, 1972, **45**, 2583.
277. U.Hahart, Ber., 1882, **15**, 898.
278. A.Onufronewicz, Ber., 1884, 17, 833.
279. A.H.Gill, Ber., 1893, **26**, 649.
280. J.Kenner and E.Witham, J.Chem.Soc., 1910, 1960.
281. P.Karrer, W.Wanrli, and E.Bidermann, Helv.Chim. Acta, 1928, 11, 233.
282. H.J.Prins, Rec.Trav.chim., 1949, **68**, 419.
283. L.V.Johnson, F.Smith, M.Stacey, and T.C.Tetlow, J.Chem.Soc., 1952, 4710.
284. C.G.Krespan, R.T.Harder, and T.T.Drysdale, J.Amer.Chem.Soc., 1961, **83**, 3424.
285. M.G.Voskanyan, Zh.A.Chobanyan, and Sh.O.Badanyan, Arm.Khim.Zhur., 1973, **26**, 159.
286. Sh.O.Badanyan, M.G.Voskanyan, and Zh.A.Chobanyan, Arm.Khim.Zhur., 1974, **27**, 852.
287. Zh.A.Chobanyan, M.G.Voskanyan, and Sh.O.Badanyan, USSR P.422 725 (1973); Byul.Izobret., 1974, No.13, 91.
288. M.G.Voskanyan, Zh.A.Chobanyan, and Sh.O.Badanyan, Arm.Khim.Zhur., 1974, **27**. 939.
289. M.G.Voskanyan, G.G.Khudoyan, Zh.A.Chobanyan, and Sh.O.Badanyan, USSR P.413 133 (1973); Byul. Izobret., 1974, No.4, 62.
290. Sh.O.Badanyan, Zh.A.Chobanyan, G.G.Khudoyan, and M.G.Voskanyan, Arm.Khim.Zhur., 1975, **28**, 467.
291. M.G.Voskanyan, Zh.A.Chobanyan, A.A.Nalbandyan, and Sh.O.Badanyan, Arm.Khim.Zhur., 1976, **29**, 156.
292. M.G.Voskanyan, Zh.A.Chobanyan, A.A.Nalbandyan, and Sh.O.Badanyan, Arm.Khim.Zhur., 1976, **29**, 430.
293. Zh.A.Chobanyan, M.G.Voskanyan, K.N.Aslanyan, and Sh.O.Badanyan, Arm.Khim.Zhur., 1976, **29**, 161.
294. J.A.Tchobanian, Conference Papers Index, 1978, 6(3).
295. M.G.Voskanyan, Zh.A.Chobanyan, and Sh.O.Badanyan, Arm.Khim.Zhur., 1979, **32**, 209.
296. L.T.Scott and C.I.De Cicco, Tetrehedron Letters, 1976, 2663.
297. F.Toda and I.Takchira, Chem.Comm., 1975, 174.
298. S.V.Sokolovskaya and L.K.Moldovanova, Khim. Geterotsikl.Soed., 1976, 998.
299. K.Buhler and D.Pearson, "Organic Syntheses" (Translated into Russian), Izd.Mir, Moscow, 1973, Vol.1, p.180.
300. C.Touguey and I.Jacques, Synthesis, 1971, 306.
301. M.M.Michel, Boussu, J.-E.Dobois, and H.M.Normant, Compt.rend., 1971, **273C**, 1270.
302. L.A.Akopyan, Dzh.I.Gezalyan, and S.G.Matsoyan, Arm.Khim.Zhur., 1975, **28**, 72.
303. T.Saegusa and Y.Ito, Synthesis, 1975, **5**, 291.
304. T.Tsuda, F.Ohoi, Y.Ito, and T.Saegusa, Chem. Comm., 1975, 327.
305. Y.Ito, Y.Indubushi, and T.Saegusa, Heterocycles, 1975, **3**, 70.
306. Y.Ito, T.Sugaya, K.Kobayashi, and T.Saegusa, Heterocycles, 1976, **4**, 1865.
307. Y.Ito, Y.Inubushi, T.Sugaya, K.Kobayashi, and T.Saegusa, Bull.Chem.Soc.Japan, 1978, **51**, 1186.
308. Y.Ito, K.Kobayashi, and T.Saegusa, Tetrahedron Letters, 1978, 2087.
309. Y.Ito, K.Kobayashi, and T.Saegusa, Heterocycles, 1978, **9**, 85.
310. Y.Ito, K.Kobayashi, and T.Saegusa, J.Amer.Chem. Soc., 1977, **99**, 3532.
311. Y.Ito, K.Kobayashi, and T.Saegusa, Tetrahedron Letters, 1979, 1039.
312. Y.Ito, K.Kobayashi, and T.Saegusa, Heterocycles, 1979, 12, 147.
313. T.Saegusa, Y.Ito, S.Kobayashi, K.Hirota, and H.Yoshioka, Tetrahedron Letters, 1966, 6121; Bull. Chem.Soc.Japan, 1969, **42**, 3310.
314. T.Saegusa, I.Murase, and Y.Ito, Tetrahedron, 1971, **27**, 3795.
315. T.Saegusa, Y.Ito, S.Kobayashi, and K.Hirota, Tetrahedron Letters, 1967, 521.
316. T.Saegusa, Y.Ito, S.Kobayashi, N.Takeda, and K.Hirota, Tetrahedron Letters, 1967, 1273; Canad. J.Chem., 1969, **47**, 1217.
317. T.Saegusa, S.Kobayashi, Y.Ito, K.Hirota, and Y.Okumura, Bull.Chem.Soc.Japan, 1968, **41**, 1638.
318. T.Saegusa, S.Kobayashi, and Y.Ito, J.Org.Chem., 1970, **35**, 2118.
319. T.Saegusa, Y.Ito, and S.Kobayashi, Tetrahedron Letters, 1968, 935.
320. T.Saegusa, Y.Ito, S.Kobayashi, and K.Horita, J.Amer.Chem.Soc., 1967, **89**, 2240.
321. T.Saegusa and I.Murase, Syn.Comm., 1972, **2**, 1.
322. T.Saegusa, I.Murase, and Y.Ito, J.Org.Chem., 1973, **38**, 1753.

323. Y.Ito, T.Konoike, S.Fujii, T.Setsuine, and T.Saegusa, Bull.Chem.Soc.Japan, 1975, **48**, 115.
324. M.Sulzbacher, Manuf.Chem.and Aerosol.News, 1973, **44**, Ref.Zhur.Khim., 1974, 9Z74.
325. T.Tsuda, K.Ueda, and T.Saegusa, Chem.Comm., 1974, 380.
326. Y.Ito, Y.Inubushi, S.Matsumura, and T.Saegusa, Bull.Chem.Soc.Japan, 1976, **49**, 573.
327. T.Tsuda, S.Sanada, and T.Saegusa, J.Organometall. Chem., 1976, **116**, 10.
328. T.Tsuda, H.Washita, and T.Saegusa, Chem.Comm., 1977, 468.
329. T.Tsuda, H.Washita, K.Watanobe, M.Miwa, and T.Saegusa, Chem.Comm., 1978, 815.
330. Y.Ito, T.Konoike, and T.Saegusa, Tetrahedron Letters, 1974, 1287.
331. T.Saegusa, Y.Ito, K.Yonezawa, Y.Inubushi, and S.Tomita, J.Amer.Chem.Soc., 1971, **93**, 4049.
332. T.Saegusa, Y.Ito, and S.Tomita, J.Amer.Chem.Soc., 1971, **93**, 5656.
333. T.Saegusa, I.Murase, and Y.Ito, J.Amer.Chem.Soc., 1972, **45**, 830.
334. T.Saegusa, I.Murase, and Y.Ito, J.Amer.Chem.Soc., 1972, **45**, 1884.
335. T.Saegusa, K.Yonezawa, I.Murase, T.Konoike, S.Tomita, and Y.Ito, J.Org.Chem., 1973, **38**, 2319.
336. Y.Ito and T.Saegusa, "Organotransition–Metal Chemistry", New York–London, 1975, p.49.
337. Y.Ito, T.Konoike, and T.Saegusa, J.Organometall. Chem., 1975, **85**, 395.
338. T.Tsuda, H.Habu, and T.Saegusa, Chem.Comm., 1974, 620.
339. T.Saegusa, Y.Ito, S.Kobayashi, and S.Tomita, Chem. Comm., 1968, 279.
340. T.Saegusa, I.Murase, M.Nakai, and Y.Ito, Chem. Comm., 1972, **45**, 3604.
341. T.Saegusa and S.Horiguchi, Polymer J., 1974, **6**, 419.
342. T.Saegusa, S.Horiguchi, and T.Tsuda, Macromolecules, 1975, **8**, 112.
343. T.Saegusa, S.Horiguchi, and T.Tsuda, Polymer J., 1976, **8**, 302.

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