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Oligomerisation Reactions of Vinyl Monomers Containing Functional Groups

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The results of studies on the oligomerisation reactions of vinyl monomers containing functional-group substituents using metal-complex catalytic systems and thermal and electrochemical methods are surveyed. The chemical reaction mechanisms are examined.
The bibliography includes 127 references.

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I. INTRODUCTION

The oligomerisation and co-oligomerisation reactions of α-olefins and 1,3-dienes, whereby it is possible to obtain a series of linear and cyclic products of potential interest to various branches of industry, have been thoroughly investigated and extensively described in the literature. The mechanisms and kinetics of these reactions, occurring in the presence of metal-complex catalytic systems, have been established.

The behaviour of olefins containing functional groups in reactions of this kind has not been studied quite so widely. Nevertheless the presence of a polar substituent in the olefin molecule alters the electron density in the double bond and is reflected in the course of the oligomerisation process.

In the present review an attempt has been made to survey the available literature data on the oligomerisation of vinyl monomers with functional groups and also on their co-oligomerisation with olefins, dienes, and trienes.

The vinyl monomers with functional groups consist mainly of α,β-unsaturated nitriles and esters as well as vinyl derivatives of silicon.

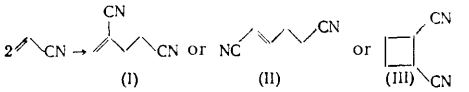
The possibility of the successful oligomerisation and co-oligomerisation of these compounds in the presence of metal-complex catalytic systems to form polyfunctional products containing a definite number of units of the initial monomer in the molecule has been demonstrated. Many of them can be of definite interest for industrial use and some are already manufactured in fairly large quantities.

The data presented in this review may prove useful in the selection of catalysts and reaction conditions ensuring high yields of the required block polymers based on vinyl monomers with functional-group substituents.

II. OLIGOMERISATION OF VINYL MONOMERS

1. Oligomerisation of Acrylonitrile

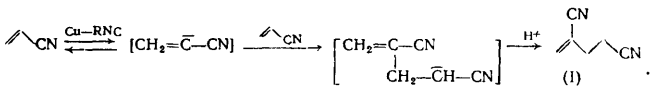
Depending on the selected conditions, the oligomerisation of acrylonitrile leads to the formation of linear dimers [α-methyleneglutaronitrile (I) and 1,4-dicyanobut-1-ene (II)], cyclic dimers [*cis*- and *trans*-1,2-dicyanocyclobutanes (III)], and higher oligomers (tri-, tetra-, and hexa-mers, etc.); the latter are formed as a rule in comparatively small amounts as admixtures to the dimeric products:



Dicyanocyclobutanes (III) are formed on thermal and photochemical cyclodimerisation of acrylonitrile. Thus, when acrylonitrile is heated to 200–300 °C, a mixture of cyclic dimers (III) is obtained in a yield of 2.5% of theoretical.[1] Approximately 4% of 1,2-dicyanocyclobutanes are formed in the photoinitiated dimerisation of acrylonitrile in the presence of sensitisers—benzophenone, 9,10-dibromoanthracene, xanthone, and others.[2] The same yield of cyclic dimers has been obtained as a result of photodimerisation in the presence of copper monochloride, which forms an intermediate coordination complex with acrylonitrile.[3] A 10% degree of conversion of acrylonitrile into 1,2-dicyanocyclobutanes has been achieved by carrying out photochemical dimerisation in the presence of molybdenum or tungsten carbonyls and reaction promoting agents, for example, triphenylphosphine.[4]

The selective formation of the linear dimer (I) has been observed in the dimerisation of acrylonitrile in the presence of binary catalytic systems consisting of copper, iron, or cobalt acetylacetonate and t-butyl- or cyclohexylisonitrile, but cyclohexylisonitrile can be used only in combination with copper and cobalt acetylacetonates, since in the presence of iron compounds it begins to polymerise appreciably lowering the catalytic activity of the system.[5,6] An obligatory condition is the presence of a proton-donating solvent, for example, a mixture of t-butyl alcohol with acetonitrile In the absence of a solvent acrylonitrile polymerises almost completely in the presence of catalytic systems of this kind. It is noteworthy that isonitrile–copper(I) oxide systems are inactive in the oligomerisation reactions of acrylonitrile.

The proposed mechanism of the dimerisation of acrylonitrile in the presence of metal–isonitrile systems involves the formation of intermediate carbanionic complexes whose existence has been confirmed by deuterium exchange reactions:[5]



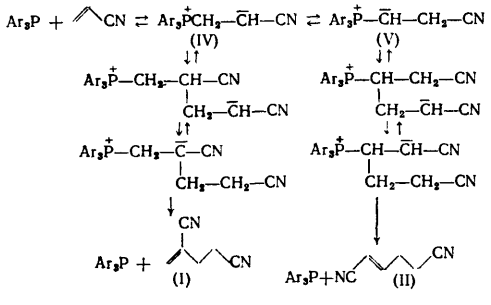
The dimerisation proceeds fairly slowly (20 h is required to obtain appreciable yields at 110 °C). The yield of the dimer (I) depends on the composition of the catalyst and reaches 50–52%.

α-Methyleneglutaronitrile is obtained in high yields (up to 68–72%) when two-component catalytic systems incorporating organic or inorganic zinc, cobalt, chromium, and aluminium salts, as well as nitrogen-containing Lewis bases (tertiary amines containing aliphatic, alicyclic, and aromatic groups or heterocyclic amines) are used.[7–11] The reaction proceeds at 20–70 °C. A small amount of the trimer (2,4,6-tricyanohex-1-ene) was found in the reaction products.

A mixture of the linear dimers (I) and (II) is formed on dimerisation of acrylonitrile in the presence of phosphorus(III) compounds.[12–31] The ratio of the isomers depends to a large extent on the nature of the organophosphorus compounds and on the solvent, temperature, and other factors. A degree of conversion of acrylonitrile not exceeding 7–9% has been achieved in dimerisation in the presence of tributyl- and triphenyl-phosphines at 45–50 °C.[12] The formation of the dimers was accompanied by the appearance of considerable amounts of the trimer (1,3,5-tricyanohex-1-ene), the hexamer, and other oligomers. The acrylonitrile hexamer 3,6-di(cyanoethyl)-1,3,6,8-tetracyano-*trans*-oct-4-ene was first detected in the oligomerisation of acrylonitrile in the presence of triphenylphosphine at 80 °C in the course of 2–4 weeks.[32]

The study of the dimerisation of acrylonitrile in the presence of triarylphosphines at 160–175 °C led to an increase in the degree of conversion of acrylonitrile to 36% and of the yield of the dimers to 85% (relative to the monomer which has reacted).[19,20] Best results have been obtained using tri(*p*-tolyl)phosphine as the catalyst. The higher nucleophilicity of methyl-substituted triarylphosphines compared with triphenylphosphine not only increases the degree of conversion of acrylonitrile but also reduces the content of the isomer (II) in the mixture of dimers from 39 to 30–32%. In dimerisation in the presence of the still more nucleophilic tri(*p*-anisyl)phosphine, the content of compound (II) falls to 9%.

The proposed mechanism of the dimerisation of acrylonitrile in the presence of tertiary phosphines includes the formation of two types of intermediate species—the phosphonium-substituted carbanion (IV) and the phosphorus ylide (V); the reactions of these species lead to the formation of α-methyleneglutaronitrile (I) and 1,4-dicyanobut-1-ene (II) respectively:[12,20]



The choice of the proton-donating solvent for the dimerisation reaction merits special attention. On passing from t-butyl alcohol to triethylsilanol, which exhibits a higher protolytic activity, the yield of the dimers increases by 20–30% other conditions being equal.[20] The absence of a source of protons promotes chain propagation and the formation of higher oligomers. In order to suppress the polymerisation reaction, it is recommended that inhibitors, namely hydroquinone, t-butylcatechol, phenothiazine, and others, be added to the reaction mixture.

A high yield of α-methyleneglutaronitrile (99%) and a satisfactory degree of conversion of acrylonitrile (up to 40%) have been achieved by carrying out continuous dimerisation in a cascade of three reactors in the presence of tri(cyclohexyl)phosphine at 80–140 °C. A mixture of t-butyl alcohol and benzene was employed as the solvent.[17]

The selective conversion of acrylonitrile into 1,4-dicyanobut-1-ene(II) takes place in the presence of catalytic amounts of the phosphonites $XArP(OR)_2$ and the phosphinites $(XAr)(Ar)POR$ or $(XAr)_2POR$, where R = alkyl or cycloalkyl, Ar = phenyl or naphthyl, and X is an electron-donating substituent: an alkyl, alkylamino-, or alkoxy-group.[25–31]

It is recommended that in this instance the dimerisation of acrylonitrile be carried out at low temperatures (below 75 °C) in the presence of a proton-donating alcoholic solvent mixed with an aprotic hydrocarbon cosolvent. An obligatory condition which must be observed to ensure a high rate of dimerisation is the employment of absolutely dry reagents and solvents, since moisture reacts with the catalyst, forming inactive compounds. When the catalyst and the mixed solvent are chosen correctly, the yield of the linear dimer (II) is 85–89% for a degree of conversion of acrylonitrile of 66–75%.[30]

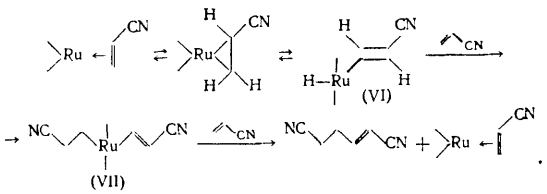
In the presence of bismuth compounds ($BiCl_3$, Bi_2O_3, $BiPh_3$, etc.) a high selectivity is achieved in the formation of 1,4-dicyanobut-1-ene (80%), but the degree of conversion of acrylonitrile is low (1–2.5%).[33] It has proved possible to enhance the catalytic effect of bismuth by adding the compounds of other metals (Sb, Co, Rh, Ir, and Ru), as a result of which the degree of conversion of acrylonitrile increases to 18%.[34–37]

The preferential formation of 1,4-dicyanobut-1-ene(II) has been observed in the dimerisation of acrylonitrile in the presence of catalytic systems containing ruthenium.[38–47] Apart from ruthenium chloride, which has come to be most widely used, the ruthenium salts of inorganic and organic acids or ruthenium complexes can be used as the main component of the catalysts. In order to accelerate the reaction and suppress the formation of side products, some workers recommend the addition of promoting agents—compounds of copper, silver, palladium, cadmium, tin, alkali metals, and alkaline earth metals.

Hydrogen plays an important role in the reaction. In the absence of hydrogen, the dimerisation of acrylonitrile in the presence of ruthenium catalysts hardly occurs. The role of hydrogen is explained by its involvement in the formation of a ruthenium hydride complex, which interacts with acrylonitrile to form the cyanoethyl complex $>Ru-CH_2-CH_2-CN$. The insertion of a second acrylonitrile molecule in the Ru–C bond leads to the dicyanobutylruthenium complex $>Ru-\underset{CN}{CH}-CH_2-CH_2-CH_2-CN$, which decomposes with liberation of 1,4-dicyanobut-1-ene. The main reaction is accompanied by the appearance of fairly large amounts of propionitrile (about 50%) and adiponitrile (up to 4%)—the products of the reaction of the cyanoethyl- and dicyanobutyl-ruthenium complexes with hydrogen.[38]

The study of the dimerisation of acrylonitrile in the presence of ruthenium catalysts in a deuterium atmosphere suggested a reaction mechanism involving the intermediate formation of the catalytically active cyanovinylruthenium hydride complex (VI) as a result of the insertion of the metal in the vinyl carbon–hydrogen bond. The interaction of the complex (VI) with a second acrylonitrile molecule leads

to the dimeric complex (VII), which decomposes with formation of 1,4-dicyanobut-1-ene and the regeneration of the catalyst:[48]

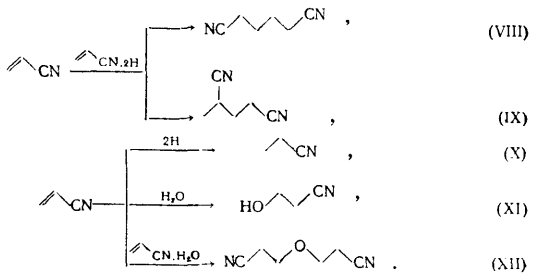


In the absence of hydrogen but in the presence of added electron-donating ligands, which form a coordinate bond with ruthenium (amines, carboxylic acids and their salts), the acrylonitrile dehydrodimerisation products—a mixture of the geometrical isomers of 1,4-dicyanobuta-1,3-diene—are formed preferentially.[49] Equimolar amounts of 1,4-dicyanobuta-1,3-diene and propionitrile have been obtained on dimerisation of acrylonitrile in the presence of catalytic platinum complexes incorporating diethylamine ligands: $(C_2H_4)Pt.(Et_2NH)Cl_2$ and $Et_2NHCH_2CH_2Pt(Et_2NH)Cl_2$.[50]

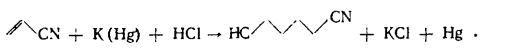
The acrylonitrile hydrodimer, namely adiponitrile (VIII), merits special attention, because it is one of the monomers used in the large-scale manufacture of nylon-6,6. Apart from the dimerisation reaction, already mentioned above, of acrylonitrile in the presence of ruthenium catalysts in an atmosphere of hydrogen, where adiponitrile is formed as an admixture to the main product (1,4-dicyanobut-1-ene),[38,51-53] it can be obtained in a mixture with another hydrodimer, namely 2-methylglutaronitrile (IX), on dimerisation of acrylonitrile in the presence of catalytic systems of three types containing iron and cobalt carbonyls:

$$Fe(CO)_5 \text{ or } Co_2(CO)_8 + \text{alkali} + H_2O;$$
$$Fe(CO)_5 \text{ or } Co_2(CO)_8 + NaBH_4 \text{ or } LiAlH_4;$$
$$Co_2(CO)_8 + H_2.$$

It is recommended that the reaction be carried out at 110 °C at a pressure of 80 atm in benzene or methanol with addition of a polymerisation inhibitor.[54] In all cases appreciable amounts of propionitrile (X) are formed in addition to the hydrodimers. In aqueous media acrylonitrile reacts partly with water to form ethylenecyanohydrin (XI) and biscyanoethyl ether (XII):



A satisfactory yield (90–100%) of adiponitrile has been achieved by dimerising acrylonitrile in the presence of Co(O) complexes, in particular $Co(N_2)(PPh_3)_3$.[55] The possibility of the selective hydrodimerisation of acrylonitrile to adiponitrile using an alkali metal amalgam has been reported:[56-58]

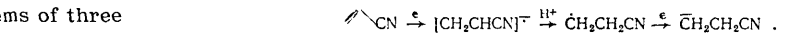


This well known method, used in preparative organic chemistry, has been tested on large-scale experimental apparatus. The course of the reaction is greatly influenced by the stability of the intermediate free radicals, the radicals generated on the surface of the amalgam being more stable than those in solution; the polymerisation of acrylonitrile is therefore not observed in this process. The yield of adiponitrile in the first runs was 60–62% and was later increased to 85–90% relative to the acrylonitrile which has reacted and finally more than 95% of adiponitrile was obtained in a polar solvent—acetonitrile with added water and a quaternary ammonium salt. The main reaction is accompanied by the appearance of small amounts of propionitrile.[58]

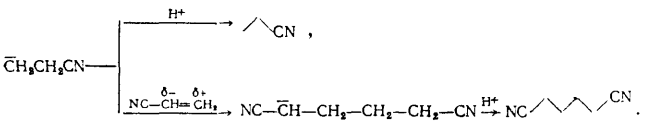
The formation of a side product (alkali metal chloride) and the high consumption of the amalgam must be regarded as disadvantages of the amalgam method for the hydrodimerisation of acrylonitrile. Studies are therefore being continued in order to improve the amalgam method and to replace potassium amalgam by the cheaper sodium amalgam, which is formed in large amounts as an intermediate in the manufacture of chlorine from caustic soda by the electrolysis of common salt. The successful completion of these studies will make it possible to combine the manufacture of adiponitrile with the electrolysis of common salt and thus ensure the supply of cheap adiponitrile.

A convenient method for the synthesis of dimeric products from the initial unsaturated compounds is that of direct cathodic hydrodimerisation. This method has been fairly extensively developed and the cathodic hydrodimerisation of acrylonitrile with formation of adiponitrile has been achieved on the industrial scale.[58-60]

In the first stage of the process a radical-anion is formed at the cathode and then rapidly transformed into a carbanion:



At a comparatively high pH of the aqueous solution and high acrylonitrile concentrations the carbanion undergoes nucleophilic addition to a second monomer molecule, forming a dimeric carbanion, which is protonated to give adiponitrile. At a low pH (less than 2) and low acrylonitrile concentrations (less than 10%) the carbanion is protonated with formation of propionitrile:



In anhydrous electrolytes higher acrylonitrile oligomers are formed.

In order to increase the yield of adiponitrile and suppress the formation of side products, it is necessary to maintain the acrylonitrile concentration in the electrolyte above 10%. With the aim of increasing the electrical conductivity and solubility of acrylonitrile, the hydrodimerisation is carried out in a solution of a quaternary ammonium salt (tetraethylammonium toluene-p-sulphonate) or in a mixture of aqueous solutions of potassium phosphate and tetraethylammonium phosphate.

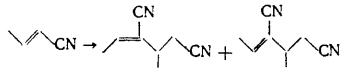
The reaction is carried out at 25–50 °C at lead or graphite cathodes using a current density of 25–100 A dm^{-2} (lead) or 4–15 A dm^{-2} (graphite). The yields with respect to the test substance and the current reach 90–93%.

The electrochemical method of synthesis of adiponitrile competes successfully with the chemical methods, which are employed under more severe conditions. At the present time industrial and large experimental plants for the electrochemical hydrodimerisation of acrylonitrile, operating in the USA, England, Japan, Belgium, and the Federal Republic of Germany, produce more than 170000 tonnes of adiponitrile

annually and the unit capacity of the plants has been raised to 90000 tonnes per annum.

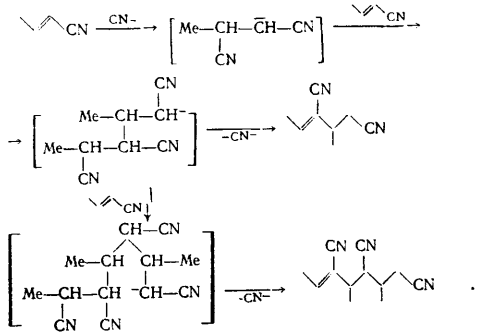
2. The Oligomerisation of α(β)-Alkyl-substituted αβ-Unsaturated Nitriles

Few studies have been devoted to the oligomerisation of αβ-unsaturated nitriles substituted in the β-position. In the investigation of the dimerisation of αβ-unsaturated carbonyl compounds and nitriles in the presence of binary catalytic systems comprising copper(I) and copper(II) compounds and isonitriles considerable attention has been devoted to the dimerisation of crotononitrile, which results in the formation of a mixture of geometrical isomers of 1,3-dicyano-2-methylpent-3-ene: [5,61]



In contrast to acrylonitrile, the dimerisation of crotononitrile proceeds readily in the presence of copper(I) oxide–t-butyl- or cyclohexyl-isonitrile systems without the need for the presence of proton-donating solvents (acrylonitrile polymerises under these conditions). At 90 °C the yield of crotononitrile dimers in the presence of such systems reaches 90% after only 1 h. [61] Copper acetylacetonate and chloride as well as copper(II) oxide can also be employed for the dimerisation of crotononitrile, but they are less active. It is of interest that the copper compound—isonitrile systems are effective only when the substituent in the β-position is a primary or secondary alkyl group. Compounds with a tertiary alkyl or aryl group in the β-position do not dimerise.

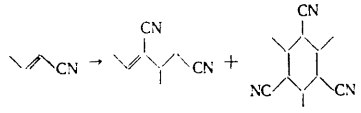
The crotononitrile dimer has been obtained in 52–54% yield together with a mixture of trimers in 33% yield in the oligomerisation of crotononitrile in the presence of tetraalkylammonium cyanides, in particular $(Et_4N)_3[Co(CN)_5]$ and $(Et_4N)_3[Co(CN)_5O_2]$. The more reactive acrylonitrile is fully polymerised in the presence of catalysts of this type. The mechanism of the oligomerisation of crotononitrile has been formulated as follows: [62]



The prolonged (up to 2 h) induction period when tris(tetraethylammonium) pentacyanocobaltates are used could not be accounted for.

Crotononitrile also oligomerises when yet another nucleophilic anionic cobalt(I) complex is employed, namely cobalt N,N′-ethylenebis(salicylideneiminate). [63] The use of this complex in the form of the sodium salt im dimethylformamide leads to the formation of the dimer (1,3-dicyano-2-methylpent-3-ene) in 68% yield and the trimer (1,3,5-tricyano-2,4-dimethylhept-5-ene) in 20% yield. In this case too acrylonitrile gives rise to a solid polymer and a small amount of α-methyleneglutaronitrile is formed only after the addition of t-butyl alcohol (a weak proton donor) (the yield of the acrylonitrile dimer is ~50 times smaller than that of the crotononitrile dimer). According to the author, acrylonitrile promotes the conversion of the active univalent cobalt complex into an inactive bivalent cobalt compound.

In the presence of the potassium–benzylpotassium catalytic system the oligomerisation of crotononitrile results in the formation of the dimer (1,3-dicyano-2-methylpent-3-ene) and a cyclic trimer (1,3,5-tricyano-2,4,6-trimethylcyclohexane): [64]



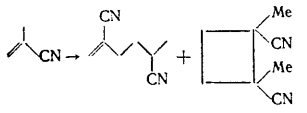
The reaction is carried out in the presence of an excess of toluene or methylcyclohexane at 110 °C. After 1 h, the degree of conversion of crotononitrile reaches 88.5%. The yield of the mixture of *cis*- and *trans*-1,3-dicyano-2-methylpent-3-enes (in proportions of 67 : 33) is 20–23%, while that of the trimer is 67–75%. When potassium is replaced by sodium, the yield of the oligomerisation products is reduced to 30–35%, other conditions being equal, although the ratio of the dimer and trimer remains unaltered.

The data presented permit the conclusion that the dimerisation of β-alkyl-substituted αβ-unsaturated nitriles requires the presence of powerful nucleophiles. The latter induce the polymerisation of acrylonitrile, but weaker nucleophilic catalysts can be used to achieve its dimerisation.

Several studies have been devoted to the oligomerisation of methacrylonitrile. A patent, [10] in which the oligomerisation of acrylonitrile is considered in detail, mentions the possibility of the oligomerisation of methacrylonitrile in the presence of catalytic systems comprising the zinc or cobalt salts of trifluoromethanesulphonic acid and triethylamine, but there are no data concerning the composition and yield of the oligomerisation products and also the degree of conversion of the initial monomer.

The possibility of obtaining α-methylene-δ-methylaldipodinitrile (a linear methacrylonitrile dimer) in the presence of a mixed catalyst containing α- or β-naphthylamine and $NiCl_2$ has been investigated. [65] The reaction is carried out at 220–230 °C. Apart from the main product, small amounts of the cyclic dimer (1,2-dicyano-1,2-dimethylcyclobutane) and a trimer, whose structure is not given by the authors, are formed under these conditions.

When methacrylonitrile is heated in the presence of polymerisaton inhibitors, a mixture of α-methylene-δ-methyladipodinitrile with cyclic dimers (*cis*- and *trans*-1,2-dicyano-1,2-dimethylcyclobutanes) is formed: [66]



Large amounts of a trimer and higher oligomers have also been detected in the reaction products. As the reaction temperature is altered, the ratio of oligomers of different structure changes within wide limits. At 340 °C the fraction of the linear dimer is about 50% of the reaction products, while at 200 °C the cyclic isomers predominate in the reaction mixture.

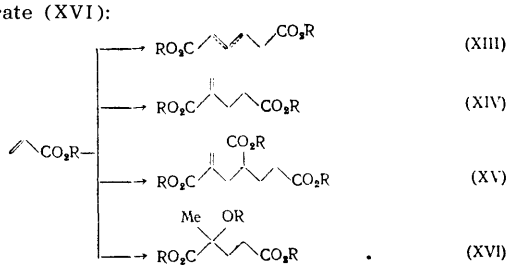
The cyclic methacrylonitrile dimer is formed in a very low yield (2%) as a result of the photodimerisation of methacrylonitrile in the presence of univalent copper. [3] Copper(I) chloride, which is readily soluble in the initial monomer, forms a coordination complex with the latter, ensuring the activation of the double bond and promoting ring closure.

The concentration of CuCl in methacrylonitrile should be not less than 8×10^{-3} M, since otherwise methacrylonitrile begins to polymerise.

Thus the oligomerisation reactions of unsaturated nitriles make it possible to obtain mainly linear dimers whose composition depends on the catalyst employed and the selected reaction conditions. Best results have been obtained using the electrochemical method for the hydrodimerisation of unsaturated monomers with functional groups.

3. The Oligomerisation of Alkyl Esters of Acrylic Acid

The oligomerisation of alkyl acrylates yields mainly three isomers: dialkyl Δ^2- or Δ^3-dihydromuconates (XIII) and dialkyl α-methyleneglutarate (XIV). In certain cases the dimerisation is accompanied by the formation of small amounts of the linear trimer (XV) and dialkyl α-alkoxy-*d*-methylglutarate (XVI):



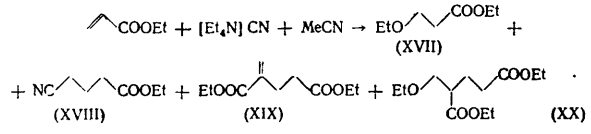
When copper–isonitrile binary systems are used, methyl acrylate is less reactive than acrylonitrile and significant results (yields of the dimer of 11%) are obtained only in the presence of the copper(I) oxide—isonitrile system and a proton-donating solvent. Without the solvent, the monomer polymerises very slowly and, when copper(I) oxide is replaced by copper or cobalt acetylacetonate, the yield of dimethyl α-methyleneglutarate falls to 1–2%.[5]

An analogous picture is observed when binary systems consisting of aluminium or zinc halides and nitrogen-containing Lewis bases are used. In this case too alkyl acrylates proved to be inert. Whereas the yield of the acrylonitrile dimers exceeds 50% in the presence of such catalysts, methyl acrylate gives rise to only 5% of dimethyl α-methyleneglutarate under identical conditions.[8]

There have been a number of reports concerning the possibility of the dimerisation of alkyl acrylates in the presence of organophosphorus compounds.[67–69] In the experiments performed with a solution of ethyl acrylate in t-butyl alcohol in the presence of triphenylphosphine a very low degree of conversion of the initial monomer into a mixture of diethyl α-methyleneglutarate and diethyl Δ^2-dihydromuconate was observed even after two weeks at 40 °C.[12]

Diethyl α-methyleneglutarate has been obtained in 67% yield when ethyl acrylate was dimerised in the presence of tributylphosphine in acetonitrile at 40–45 °C.[67] When tris(ethoxycarbonylethyl)phosphine was used, the yield of the diester fell somewhat, but remained fairly high (47%). The only side product in these reactions is the trimer, formed in small amounts.

A complex mixture of oligomerisaton products is obtained when less active catalysts, namely tetra-alkylammonium cyanides, are used:[62]

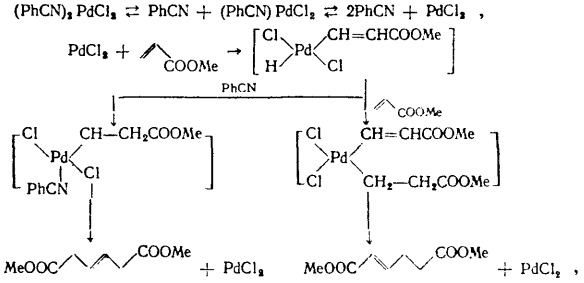


When the reactor is cooled to 5 °C, it is possible to obtain solely compounds (XVII) and (XX). Their formation shows that the ethoxy-group is displaced from the initial product under the reaction conditions with its subsequent addition to the activated double bond. The proton necessary for the formation of compound (XVII) is obtained following the Hoffmann cleavage of the tetraethylammonium cation. The yield of the dimer (XIX) is very low; compound (XVIII) is formed as a result of the addition of acetonitrile to the olefin via the Michael reaction, which the authors believe to be catalysed by the ethoxide anion (tetraethylammonium cyanides do not catalyse this reaction).

The anionic complex cobalt N,N'-ethylenebis-salicylideneiminate promotes the conversion of ethyl acrylate into diethyl α-methyleneglutarate with an insignificant admixture of the trimer.[63] After 10 h, the degree of conversion of the initial monomer reaches 40%. The anionic oligomerisation of methyl and ethyl acrylates has been investigated in the presence of sodium methoxide or ethoxide in anhydrous methanol and ethanol respectively.[70] In both cases the degree of conversion of the monomers is 80–90% after 24 h at the boiling point; in addition to dialkyl α-methyleneglutarate, the corresponding saturated alkoxy-derivative (XVI) was detected in the reaction products. It is noteworthy that in the case of ethyl acrylate the amount of unsaturated dimer obtained is greater than for methyl acrylate.

The preferential formation of dimethyl Δ^2-dihydromuconate is observed when ruthenium or rhodium trichloride trihydrate is used.[71] It is recommended that the reaction be performed in methanol or tetrahydrofuran. A temperature of 140 °C was sufficient for the attainment of a high yield of the dimer in the presence of $RhCl_3 \cdot 3H_2O$ and the formation of higher oligomers was not observed. $RuCl_3$ is less active in this reaction and 48% of the dimer was obtained only at 210 °C. The promoting influence of ethylene, whose addition makes it possible to reduce the reaction temperature to 150 °C and to increase the yield of the dimer to 56%, was unexpected Admittedly a small amount of methyl pent-3-enoate appears in the reaction products under these conditions as a result of the co-oligomerisation of ethylene with methyl acrylate.

Bivalent palladium complexes proved to be fairly active in the dimerisation reactions of alkyl acrylates.[72,73] The readily soluble, non-hygroscopic dichlorobisbenzonitrile complex, which catalyses the dimerisation of methyl acrylate in accordance with the mechanism



is very convenient for this purpose. After 23 h at 113 °C, the degree of conversion of methyl acrylate reaches 67% and the selectivity with respect to linear dimers exceeds 90%. The ratio of the Δ^2- and Δ^3-isomers varies in the range 50 : 50–67 : 33 depending on the reaction conditions.[72]

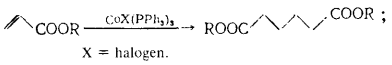
The high process selectivity led investigators to seek ways of increasing the effectiveness of palladium catalysts. The inadequate degree of conversion of alkyl acrylates (67%) is attributed to the comparatively rapid loss of activity by dichlorobis(benzonitrile)palladium.[74]

It was found that the addition of *p*-benzoquinone prevents not only the reductive deactivation of the catalysts but also the radical polymerisation of the monomer; the degree of conversion of the initial monomer increases to 75–92% and the necessary reaction temperature falls to 81 °C. It has been suggested that complexes more reactive than the initial complex may be formed between palladium phenoxide and the benzoquinone reaction products.[74]

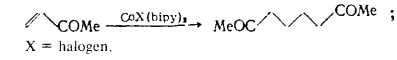
Silver tetrafluoroborate exerts an even stronger activating effect on the catalytic $PdCl_2$ complexes.[75] Depending on the catalyst/$AgBF_4$ ratio, the rate of dimerisation of methyl acrylate increases by 1–2 orders of magnitude and the selectivity changes in favour of dimethyl Δ^2-dihydromuconate. $AgBF_4$ has an analogous effect also on the dichlorophosphine-palladium complexes $(PhP)_2PdCl_2$ and $(Bu_3P)_2PdCl_2$, which hardly catalyse the dimerisation of alkyl acrylates in the absence of this additive. The activated complexes are especially selective and it is possible to obtain with their aid a virtually pure Δ^2-isomer (the admixture of dimethyl Δ^3-dihydromuconate does not exceed 1–3%).

It has been suggested that silver tetrafluoroborate promotes the formation of free coordination-unsaturated centres in the catalytically active complex as a result of the partial dissociation of the neutral ligand, which is confirmed by the impossibility of activating by $AgBF_4$ complexes containing chelating ligands such as 1,2-bis(diphenylphosphino)-ethane and 1,2-bis(N,N-dimethylamino(ethane.

In the presence of triphenylphosphine complexes of cobalt in protic solvents, alkyl acrylates undergo reductive dimerisation with formation of the corresponding dialkyl adipates:

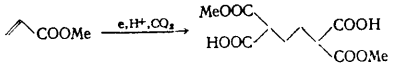


The hydrodimerisation of methyl vinyl ketone to octane-2,7-dione takes place successfully in the presence of cobalt complexes containing bipyridyl ligands:[76]



The electrochemical hydrodimerisation of alkyl acrylates, which takes place exclusively "tail to tail", is characterised by a high selectivity and satisfactory yields.[61,77] The yield of the hydrodimers depends on the composition of the electrolyte and the nature of the alkyl moiety in the ester group (it decreases with increased number of carbon atoms). Thus in an alkaline solution the yield of the methyl acrylate hydrodimer reaches 73%, while only 40% of diethyl adipate is formed from ethyl acrylate; in order to increase the yield of adipate to 75%, it is necessary to raise the electrical conductivity of the solution with the aid of quaternary ammonium salts. It has been altogether impossible to obtain the butyl acrylate hydrodimer by the electrochemical procedure.[77]

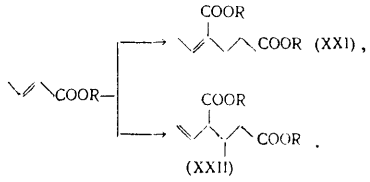
A very interesting product, namely the dimethyl ester of butane-1,1,4,4-tetracarboxylic acid, has been obtained in yields up to 47% by the electrochemical reduction of methyl acrylate in the presence of carbon dioxide:[78]



Great importance must be attributed to reactions of this type, since they lead to yet another possibility for the direct utilisation of carbon dioxide in organic synthesis.

4. Oligomerisation of the Alkyl Esters of Crotonic Acid

Depending on the catalyst, the oligomerisation of alkyl crotonates proceeds with formation of the dialkyl esters of 2-methylpent-3(or 4)-ene-1,3-dicarboxylic acid—compounds (XXI) and (XXII) respectively:



Some of the catalytic systems used for crotononitrile are suitable for these reactions. A mixture of the *cis*- and *trans*-isomers of compound (XXI) is formed from alkyl crotonates in the presence of the copper(I) oxide–cyclohexylisonitrile system in a fairly satisfactory yield (albeit lower than in the case of crotononitrile).[61,79] At 90 °C the yield of the methyl crotonate dimers reaches 70% after 3 h (the ratio of the *cis*- and *trans*-isomers in the mixture is 80 : 20). A characteristic feature is the need to employ a large excess of cyclohexylisonitrile relative to copper(I) oxide. When cyclohexylisonitrile is replaced by t-butylisonitrile, the reaction slows down (the yield of the dimers is only 50% after 12 h). Under these conditions, ethyl crotonate is more inert (the yield of the dimers does not exceed 15% after 14 h even at 100 °C).

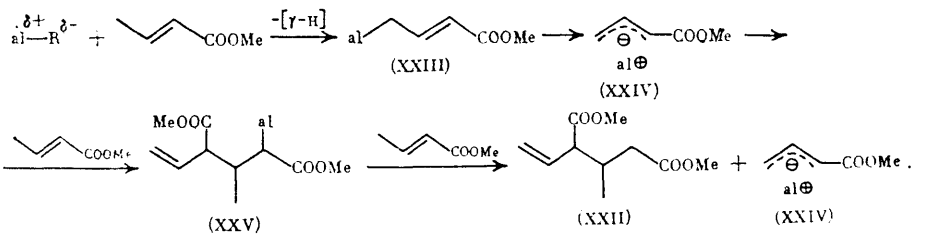
In the presence of tetraethylammonium cyanide in acetonitrile, ethyl crotonate dimerises with formation of 67% of the diethyl ester (XXI).[62]

Ethyl crotonate dimerises very rapidly and almost quantitatively at 110 °C in the presence of the potassium–benzylpotassium catalytic system in solution in toluene.[80] In contrast to crotononitrile, ethyl crotonate dimerises very selectively under these conditions—90% of the product consists of the dimer (XXI) and the content of the *cis*-isomer is higher than in the case of crotononitrile (81% instead of 67%).

A very pure dimethyl ester (XXII) has been obtained in a study of the oligomerisation of methyl crotonate in the presence of the trimethyl- or triethylaluminium–sparteine systems.[81,82] A mixture of compounds (XXI) and (XXII) in proportions of 11 : 73–54 : 34 (depending on the solvent employed) with an admixture of 12–16% of the diastereoisomers (XXII) is formed in the presence of the isobutylaluminium–sparteine system.

A mixture of compounds (XXI) and (XXII) in proportions of 97 : 3–69 : 31 has been obtained using the triethylaluminium–triethylamine catalytic complex; the content of the dimer (XXI) increases with reaction time, while the amount of compound (XXII) diminishes simultaneously, which shows that the dimer (XXI) is formed as a result of the isomerisation of compounds (XXII). It is noteworthy that acrylonitrile and methyl methacrylate polymerise fully in the presence of such catalytic systems.

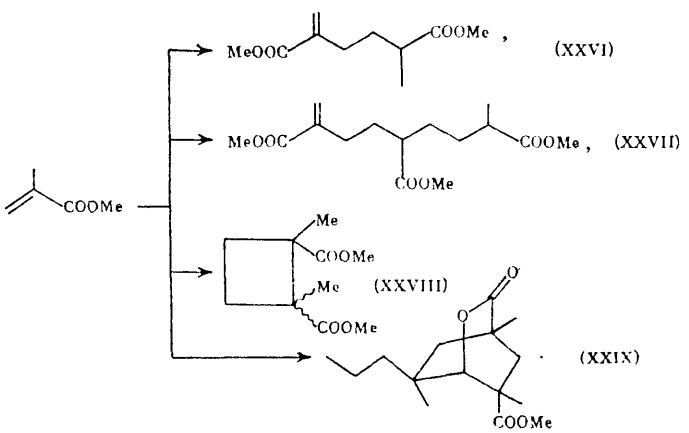
The author showed by experiments with methyl crotonate deuteriated in the α- and γ-positions that the reaction is initiated by the abstraction of the acid γ-proton from methyl crotonate by the catalytic complex and proposed the following reaction mechanism:



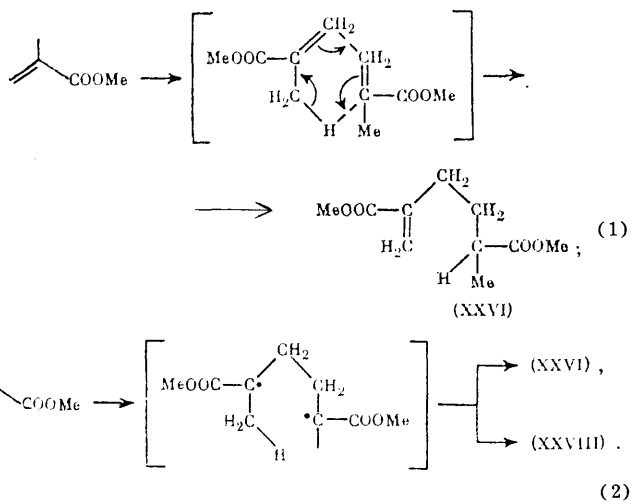
Here al represents the Et_2Al–sparteine residue. The abstraction of the γ-proton results in the formation of the intermediate complex (XXIII), which can have the delocalised structure (XXIV). This complex attacks the methyl crotonate molecule with formation of the adduct (XXV), which is converted into the dimer (XXII) with regeneration of the active complex (XXIV).

5. Oligomerisation of Alkyl Methacrylates

The esters of methacrylic acid and in the first place methyl methacrylate are known to be widely used in the manufacture of film-forming polymers. The appearance of oligomers of different structure in the course of the polymerisation of methacrylates stimulated investigators to study the conditions and mechanism of the formation of oligomers during the heat treatment of the alkyl esters of methacrylic acid. The probability of the formation of the following methyl methacrylate oligomers has been demonstrated: dimethyl 1-methylene-4-methyladipate (XXVI), trimethyl non-1-ene-2,5,8-tricarboxylate (XXVII), dimethyl *cis*- and *trans*-1,2-dimethylcyclobutane-1,2-dicarboxylates (XXVIII), and a cyclic trimer—methyl 4,6,7-trimethyl-3-oxo-7-propyl-2-oxabicyclo[2.2.2]octane-6-carboxylate (XXIX):



In one of the early studies[66] it was shown that, when methyl methacrylate is heated for 12 h at 225 °C, mainly the linear dimer (XXVI) and the linear trimer (XXVII) are obtained. The same products have been synthesised by the thermal oligomerisation of methyl methacrylate at 100°, 120°, and 130 °C [83] (we may recall that an appreciable proportion of the methacrylonitrile reaction products consist of cyclic dimers under these conditions). Two possible dimerisation mechanisms have been considered: the "ene-enophilic" (1) and the biradical (2) mechanisms:



It has been suggested[83] that in the latter case chain termination and disproportionation of the biradical take place in the course of the reaction with formation of the linear dimer (XXVI) and that only a small proportion of the methacrylate cyclises to the tetrasubstituted cyclobutane (XXVIII).

However, on the basis of the study of the kinetics of this process, it was concluded that the formation of compound (XXVIII) agrees with the biradical initiation mechanism, while the linear dimer and trimer are obtained via the "ene-enophilic" mechanism.[84]

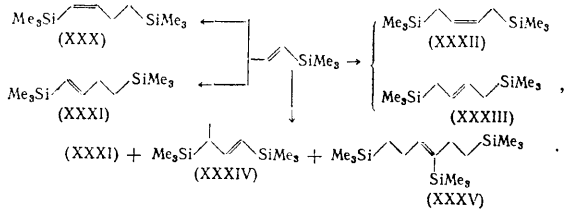
The methyl methacrylate trimer, obtained under the influence of diethylaluminium chloride in the presence of 2,2'-azobisisobutyronitrile as the initiator, has been identified as the bicyclic lactone (XXIX).[85]

6. Oligomerisation of Vinyl Derivatives of Silicon

The oligomerisation of vinyl derivatives of silicon with formation of di-, tetra- and octa-mers was first mentioned in connection with the study of the polymerisation of these monomers.[86,87] The specific synthesis of the linear dimers of trimethylvinyl- and triethylvinyl-silanes was achieved in 1961 by the reaction of the monomers with triisobutylaluminium.[88] For a number of years no studies on these lines were performed and it is only recently that reports have appeared concerning the results of the investigation of the oligomerisation of vinylsilanes in the presence of metal complex systems.[89,90]

Three-component systems consisting of nickel, cobalt, or titanium compounds, as organoaluminium reductant, and triphenylphosphine or triphenylstibine as the electron-donating additive have been investigated. The nickel and cobalt compounds have been used as chelates and the titanium compound was tetrabutoxytitanium. In the

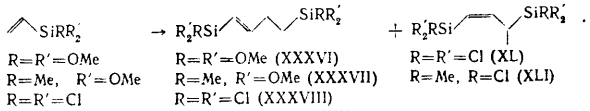
presence of such metal complex catalysts trimethylvinylsilanes give rise mainly to disilylbutenes with different configurations and with different positions of the double bond:



In the presence of the system prepared by treating cobalt 8-hydroxyquinolate with triethylaluminium in the presence of triphenylphosphine, trimethylvinylsilane dimerises with formation of 1,4-bis(trimethylsilyl)-*cis*-but-1-ene (XXX) in 30% yield relative to the monomer which has reacted. The replacement of triphenylphosphine by triphenylstibine leads to the formation of the *trans*-isomer (XXXI) in the same yield. The metal complex system comprising nickel acetylacetonate, triethylaluminium, and triphenylphosphine in the absence of a solvent showed no catalytic activity in relation to vinylsilanes, but the use of dichloroethylene as the solvent led to the formation of a mixture of compounds (XXXII) and (XXXIII) in proportions of 1:1 and in 86% yield. When the organoaluminium reductant is replaced by trichlorosilane, the dimer (XXX) is obtained in 30% yield.

Whereas the nickel and cobalt catalysts make it possible to obtain only unbranched trimethylvinylsilane dimers, the system comprising tetrabutoxytitanium, triethylaluminium and triphenylphosphine promotes the formation of the branched dimer *trans*-1,3-bis(trimethylsilyl)-3-methylprop-1-ene (XXXIV) together with the linear dimer (XXXI). In addition the formation of the linear trimer 1,2,3-tris(trimethylsilyl)hex-3-ene (XXXV) has been noted. The oligomers are formed in the proportions (XXX):(XXXIV):(XXXV) = 2:3:1. It is noteworthy that the titanium system is the only one in the presence of which it has been possible to detect the formation of the trimethylvinylsilane trimer.

The oligomerisation of trimethoxyvinyl- dimethoxymethylvinyl-, trichlorovinyl-, and dichloromethylvinyl-silanes in the presence of the system comprising tetrabutoxytitanium, triethylaluminium and triphenylphosphine has been investigated at 100–120 °C (contact time 6–10 h): [90]

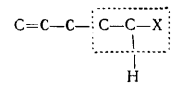


The dimerisation of methoxy-derivatives of vinylsilanes proceeds with a high selectivity. The *trans*-isomers [compounds (XXXVI) and (XXXVII)] are obtained in a yield up to 80% for a degree of conversion of the monomers of 49%. Chloro-substituted vinylsilanes dimerise less vigorously in the presence of the titanium system. Trichlorovinylsilane gives rise to a mixture of the *cis*- and *trans*-isomers (XXXVIII) and (XL) in proportions of 1:1, in 35% yield, and with a degree of conversion of the monomer of 42%. A mixture of dichloromethylvinylsilane dimers (XXXIX) and (XLI) in proportions of 1:2 is obtained in the same yield (35%).

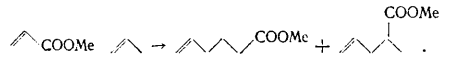
III. CO-OLIGOMERISATION OF VINYL MONOMERS WITH UNSATURATED HYDROCARBONS

1. Co-oligomerisation with Olefins

In the early stages of the investigation vinyl monomers with functional groups were subjected to a high-temperature (200–300 °C) thermal interaction with olefins. [91,92] A study was made of the behaviour of a large number of enophiles (acrylonitrile and methacrylonitrile, methyl esters of acrylic and methacrylic acids, acrylic acid, etc.) with propene, butenes, isobutene, and certain higher olefins. [91] In all cases the reaction results in the formation of adducts of the type



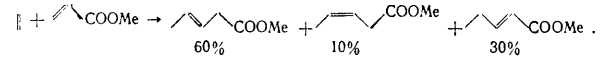
[the C–C atoms printed bold indicate the initial position of the double bond in the olefin, H is the hydrogen atom which has migrated, and C–C–X is the skeleton of the enophile with the activating functional group X (CN, COOR, etc.)]. A higher yield of adducts (up to 49%) is attained when 1,1-disubstituted ethylenes are used, for example, isobutene, while in the case of normal olefins the yield is sharply reduced (down to 18% for propene and 4% for but-2-ene). Furthermore, when normal olefins are employed, the formation of a branched adduct, whose amount increases with the number of carbon atoms in the olefin, is observed: [92]



In the codimerisation of methyl acrylate with n-hept-1-ene, the amount of the branched adduct is 25% of the total adducts.

The use of catalysts makes it possible to carry out the codimerisation under milder conditions. In the presence of ruthenium chloride, methyl acrylate reacts with an excess of ethylene at 150 °C to form a mixture of codimers (esters of pent-3-enoic acid, yield 47%) and esters of acids containing seven (12%) and nine (9%) carbon atoms. [71] A methyl acrylate dimer (yield 23%) and butene were also found among the reaction products. The same products have been obtained in the presence of rhodium chloride at 120 °C.

Three isomeric products of the codimerisation of ethylene with methyl acrylate in an overall yield of 47% relative to the methyl acrylate which has reacted are formed in the presence of dichlorobis(benzonitrile)palladium at 105 °C: [72]



An analogous mixture but with a lower yield has been obtained using the complex $[C_2H_4PdCl_2]_2$ as the catalyst. [93]

Lewis acids exert a particularly favourable effect on reactions of this kind, permitting a reduction of the reaction temperature to 25 °C and even lower. [94–99] The catalytic effect of a large number of such compounds has been studied: BF_3, BCl_3, BBr_3, $SbCl_5$, $TiCl_4$, $SnCl_4$, $AlCl_3$, and alkylaluminium chlorides ($EtAlCl_2$, Et_2AlCl, Et_3Al, $Et_3Al_2Cl_3$, Me_2AlCl, etc.). The choice of the catalyst depends on the reactivity of the enophile. Esters, including acrylates and crotonates, require stronger Lewis acids—$AlCl_3$ or $EtAlCl_2$. Aldehydes and ketones are much more reactive—in particular acrolein and crotonaldehyde react successfully with olefins in the presence of weaker Lewis acids—$ZnCl_2$ and Me_2AlCl. The use of alkylaluminium chlorides makes it

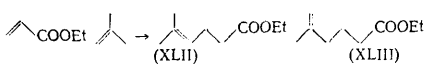
possible to avoid the proton-initiated side reactions (polymerisation of the olefin, isomerisation of the double bond in the olefin and in the co-oligomerisation products).

The results of the co-oligomerisation of vinyl monomers having functional groups with olefins depend not only on the reactivity of the enophile but also on the structure of the olefin. The following reactivity series has been found for olefins in co-oligomerisation reactions catalysed by Lewis acids: 1,1-di- > tri- > tetra- ≫ mono- > 1,2-di-substituted ethylenes.[98] As a consequence of the inadequate reactivity of long-chain olefins, for example oct-1-ene, even the presence of a strong Lewis acid ($AlCl_3$) is ineffective in the interaction of such olefins with acrylates. In such cases the addition of NaCl and KCl to $AlCl_3$ has been found to have a positive effect, permitting the formation of a codimer of methyl acrylate and oct-1-ene-, namely methyl undec-5-enoate, in 40% yield. The admixture of the unbranched ester does not exceed 4%.[96]

A satisfactory treatment of the mechanism of the co-oligomerisation reactions between vinyl monomers having functional groups and olefins in the presence of Lewis acids has not so far been achieved. According to a preliminary assessment, the interaction of the olefin with the enophile proceeds via a stage involving the formation of a complex between the enophile and the Lewis acid via a negatively charged oxygen or nitrogen atom in the enophile molecule. The activated molecule is also attacked by the other reactant in the mixture with formation of an adduct.[99]

The composition of the co-oligomerisation products formed depends not only on the structure of the initial monomers but also on the reaction conditions. In certain cases the results obtained by different workers investigating the behaviour of the same compounds under identical conditions proved to be contradictory. Thus it has been stated[100] that the co-oligomerisation of methyl acrylate with olefins in the presence of $AlCl_3$ leads to the corresponding substituted cyclobutanes. However, another investigator[95] obtained linear adducts of methyl acrylate with olefins (2-ethylbut-1-ene and methylpent-1-ene) in the presence of the same catalyst.

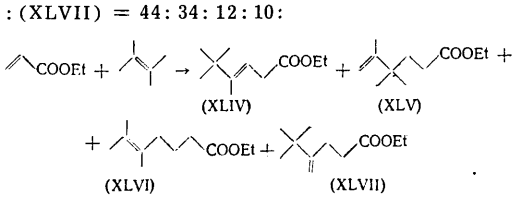
The formation of linear co-oligomers of ethyl acrylate with isobutene in the presence of $AlCl_3$ has been noted.[94] The composition of the products obtained under these conditions depends greatly on the reaction medium. The ethyl esters of 5-methylhex-4-enoic acid (XLII) and 5-methylenehexanoic acid (XLIII) are obtained in proportions of 8:1 in a mixture of dichloroethane and nitromethane:



(XLII) (XLIII)

Only the isomer (XLIII) is obtained in dry benzene.

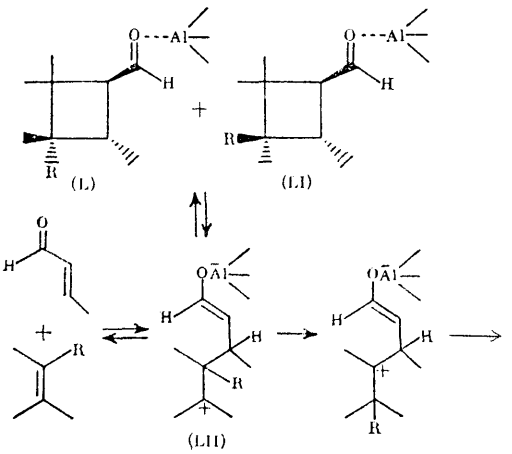
The interaction of ethyl acrylate with 2,3-dimethylbut-2-ene in a dichloroethane–nitromethane mixture led to the formation of four codimers in the proportions (XLIV):(XLV):(XLVI):(XLVII) = 44:34:12:10:

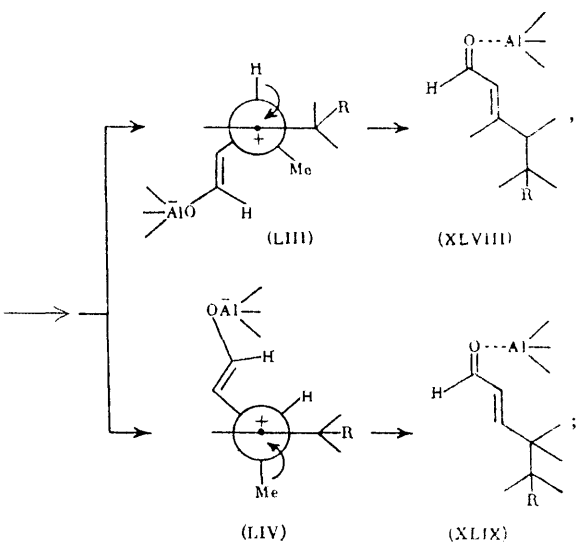


(XLIV) (XLV) (XLVI) (XLVII)

In dry benzene these monomers reacted more selectively to form compound (XLV) (only trace amounts of other isomers were found in the reaction products).

Linear and cyclic products, whose composition depends greatly on the reaction temperature, have been obtained by the reaction of αβ-unsaturated aldehydes and ketones with olefins in the presence of $EtAlCl_2$.[97] For example at 0 °C in benzene the interaction of crotonaldehyde with 2-methylbut-2-ene leads to the formation of 63% of the codimer (XLVIIIa) and 17% of the codimer (XLIXa). A mixture of 81% of cyclobutane (La), 7% of cyclobutane (Lla), 10% of the codimer (XLVIIIa), and 2% of compound (XLIXa) has been obtained at −80 °C in an overall yield of 77%. It has been suggested that the reaction proceeds via a stage involving the formation of the intermediate zwitter-ion (LIIa):

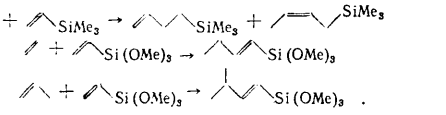




R = H (a), Me (b).

When 2-methylbut-2-ene was replaced by 2,3-dimethylbut-2-ene, the picture changed somewhat. At 25 °C the formation of only the codimer (XLIXb) in 69% yield was noted. The cyclobutane (Lb) and the codimer (XLIXb) were obtained in yields of 60% and 22% respectively in the temperature range from −80° to −40 °C. The absence of compound (XLVIIIb) is explained by the strong steric interaction between the methyl and t-butyl groups in the conformer (LIIIb).

Trimethylvinyl- and trimethoxyvinyl-silanes react with ethylene and propene in the presence of catalytic systems consisting of cobalt or titanium compounds, triphenylphosphine, and triethylaluminium in the molar proportions 1 : 1 : 4 with formation of the corresponding codimers:[101]



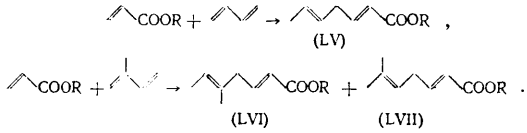
At 120 °C and for a contact time of 8–9 h the yield of the trimethylvinylsilane codimers with ethylene reaches 50% for a degree of conversion of the monomers of 65%. The codimer of trimethoxyvinylsilane and ethylene has been obtained in 36% yield for a degree of the conversion of the monomer of 80% in the presence of a catalyst containing tetrabutoxytitanium, triphenylphosphine, and triethylaluminium.

In the interaction of trimethoxysilane with propene the yield of the dimer does not exceed 28% and the degree of conversion of the monomer is 31%.

In all the reactions described, 10–25% of the products of the linear dimerisation of vinylsilanes were formed together with the codimers; the dimerisation of α-olefins has not been observed.

2. Co-oligomerisation of the Alkyl Esters of αβ-Unsaturated Carboxylic Acids with Dienes, and Trienes

The co-oligomerisation with dienes has been investigated in fair detail. In the early studies devoted to the co-oligomerisation of alkyl acrylates with buta-1,3-diene and isoprene the corresponding linear dienes were obtained and the structures of the alkyl esters of hepta-4,6-dienoic and 6-methylhepta-4,6-dienoic acids respectively were attributed to them.[102–104] However, it was subsequently shown that the alkyl esters of hepta-2,5-dienoic acid (LV) or 5-methylhepta-2,5-dienoic acid (LVI) and 6-methylhepta-2,5-dienoic acid (LVII) are formed:[105]



When cobalt acetylacetonate and triethylaluminium are used as the catalytic system, the yield of the co-oligomers of butadiene with alkyl acrylates is 20–30% and in the case of isoprene it amounts to 35–45%. The esters of hepta-3,5-dienoic acid (2–3%) and oligomers with a high molecular weight have been detected in the reaction products.

Conditions have been found for the codimerisation of isoprene with methyl acrylate whereby it is possible to obtain a mixture of *cis*- and *trans*-6-methylhepta-2,5-dienoic acids in 70–80% yield relative to the methyl acrylate which has reacted for a degree of conversion of isoprene of 70–80% and of methyl acrylate of 90–95% in the presence of catalytic systems incorporating cobalt(II) acetylacetonate, and organoaluminium reductant, and an electron-donating modifying agent.[106] Apart from triethylaluminium, which is most widely employed, tris(3-methylhepta-4,6-dienyl)aluminium and tris(cyclohexenylethyl)aluminium have been used, as reductants, because they do not ignite on contact with air and water and ensure a higher yield of co-oligomers. Triphenylphosphine, triphenylstibine, and triphenoxystibine proved to be the best modifying agents. The ratio of the *cis*- and *trans*-isomers (~2 : 1) is independent of the catalyst and the reaction conditions. Small amounts (2–5%) of a cyclic adduct, the methyl ester of cyclohex-3-ene-1-carboxylic acid, were found in the reaction products. The content of higher oligomers did not exceed 2–5%.

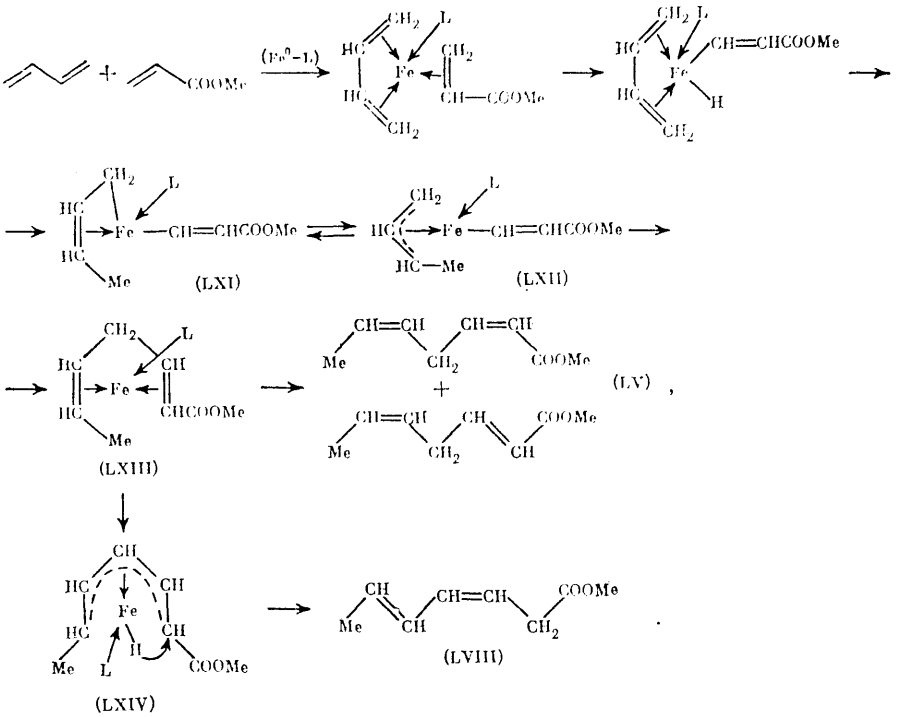
The behaviour of 1,3-dienes and alkyl acrylates in the presence of iron-containing complex catalysts has been studied in very great detail.[107–113] As a result of the co-oligomerisation of buta-1,3-diene with methyl acrylate in the presence of systems comprising iron acetylacetonate and trialkylaluminium, a mixture of the methyl esters of hepta-2,5-dienoic acid and hepta-3,5-dienoic acid (LVIII) is formed with the former predominating (80–87%), compound (LVIII) being produced as a result of the isomerisation of the ester (LV), which could be prevented in certain cases.[107,108] In addition, insignificant amounts of the methyl esters of hepta-4,6-dienoic acid and cyclohex-3-ene-1-carboxylic acid (LIX) have been found. The overall yield of codimers does not exceed 34–35% relative to the initial methyl acrylate. The optimum temperature range is 60–90 °C, since at lower temperatures the degree of conversion of the initial monomers is insignificant, while at higher temperatures cyclodimerisation begins to predominate. The ratio of the initial reactants has little influence on the yield of the required products, while the ratio Al : Fe has a significant effect on the process selectivity. The addition of powerful electron-donating compounds, namely amines, phosphines, and phosphites, which increase the activity of the catalyst, has a considerable effect. As a rule, the presence of these ligands in the reaction medium promotes the formation of the cyclic dimer. The best yields of linear codimers have been obtained using triphenylstibine Ph_3Sb and triphenyl antimonite $(PhO)_3Sb$.[109]

The degree of conversion can be altered and the codimerisation can be directed towards the formation of a particular product also with the aid of solvents. In solution in benzene the degree of conversion of the monomers reaches 95–100%, but most of them are converted into higher oligomers and the yield of codimers varies in the range 10–50% depending on the modifying agent. The selectivity of the codimerisation carried out using ethers as solvent is very high. In this case the yield of the geometrical isomers of the methyl esters of hepta-2,5-dienoic acid reaches 100% relative to the methyl acrylate which has reacted, but the degree of conversion of the monomers falls to 45–55%.[109] The combination of methylene chloride (solvent) with pyridine (electron donor) makes it possible to obtain the virtually pure (93.6%) cyclic codimer (LIX).

The authors explain the high selectivity of the reaction in ethers, particularly in tetrahydrofuran, by the fact that the ether, which is an active two-electron ligand, creates steric hindrance to the approach of the codimer molecules to the metal, while the sterically less hindered monomer molecules are coordinated without special difficulty.

The influence of the addition of copper, cobalt, nickel, manganese, and lanthanide (La, Ce, Eu, Tb, Dy, and Sm) acetylacetonates on the activity and selectivity of the catalytic system $Fe(acac)_3$–$SbPh_3$–$AlEt_3$ has been investigated.[110] With the exception of $Sm(acac)_3$, which increases the yield of the co-oligomerisation products by 12.5%, the derivatives of the other elements not only had a negative effect on the yield of the co-oligomers but also promoted the appearance, together with the esters of hepta-2,5-dienoic acid, of the ester of the conjugated hepta-3,5-dienoic acid and the cyclic adduct (LIX). Depending on the nature of the added metal and its amount, it is possible to obtain the conjugated ester or the cyclic adduct in a virtually pure form (98.5–100%), but in a low yield.

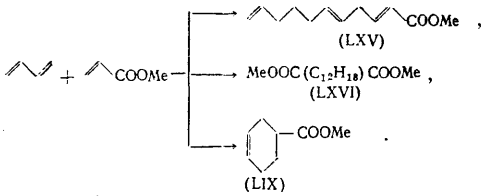
Experiments with deuterated monomers suggested the following mechanism of the codimerisation reaction:[107,111,112]



The interaction of butadiene with methyl acrylate includes the stage involving the oxidative addition of methyl acrylate to the iron atom, which leads to the hydride complex (LX), within which a proton is transferred to the activated butadiene molecule; isomerisation results in the formation of the σ,π-allyl complex (LXII). The subsequent dimerisation of the coordinated ligands leads to the formation of a new intermediate complex (LXIII); in the presence of an excess of the monomers the latter decomposes with formation of the stereoisomeric methyl esters of hepta-2,5-dienoic acid and the initial complex. In benzene (instead of tetrahydrofuran) solution the final reaction product is the isomer (LVIII) with conjugated double bonds, whose formation proceeds via the hydride complex (LXIV). The low process selectivity in the formation of codimers in benzene solution can be accounted for by the involvement of the resulting conjugated ester in subsequent reactions, leading to higher oligomers.

The co-oligomerisation of acrylic and methacrylic acids with an excess of 1,3-dienes in the presence of zerovalent nickel complexes leads to other products, formed from two and more molecules of the initial monomers. The catalyst is prepared by reducing nickel acetylacetonate (or other nickel salts) with an organoaluminium reductant in the presence of butadiene and an electron-donating organophosphorus modifying agent (phosphine or phosphite) with the addition of an inert diluent—benzene, toluene or other hydrocarbons.[114,115]

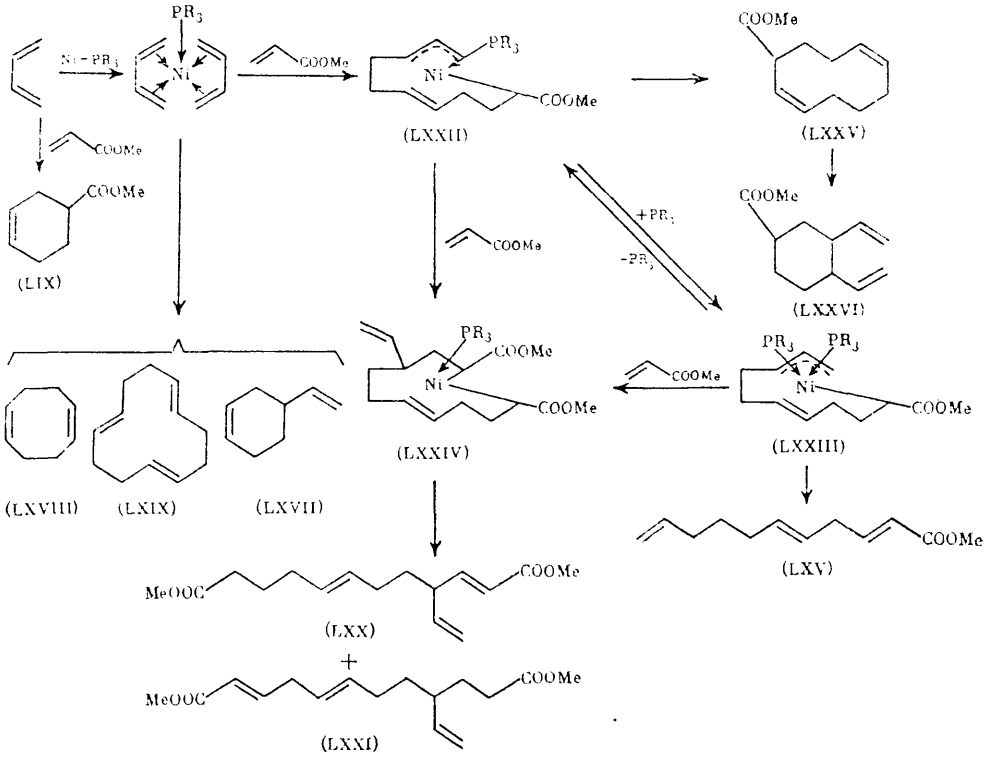
The available data on the composition of the co-oligomerisation products are contradictory. Thus it has been stated[115] that the co-oligomerisation of methyl acrylate with buta-1,3-diene at 120–165 °C leads to the formation of the methyl esters of undeca-2,5,10-trienoic acid (LXV) and cyclohex-3-ene-1-carboxylic acid (LIX), as well as the dimethyl ester of dodecatrienedicarboxylic acid (LXVI) in yields of 40.3, 8.2, and 46.5% respectively:



Other workers[116,117] obtained under the same conditions a mixture containing methyl undeca-2,5,10-trienate (LXV), 4-vinylcyclohexene (LXVII), cyclo-octa-1,5-diene (LXVIII), *trans, trans, trans*-cyclododeca-1,5,9-triene (LXIX), methyl cyclohex-3-ene-1-carboxylate (LIX), methyl 4-vinyldodeca-2,7-dienedioate (LXX) and methyl 4-vinyldodeca-7,10-dienedioate (LXXI). The yield of compound (LXV) varies in the range 15–25%.

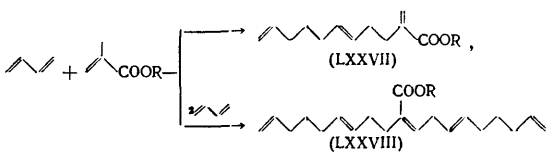
Extensive studies have been made on the influence of the structure of electron-donating modifying agents, organoaluminium reductants, and solvents on the yield and composition of the products of the co-oligomerisation of methyl acrylate with butadiene.[116] The highest yield of the ester of undeca-2,5,10-trienoic acid(LXV) (75%) has been obtained in the presence of a catalyst consisting of nickel acetylacetonate, triphenylphosphine, and tris(3-methyl-hepta-4,6-dienyl)aluminium in proportions of 1 : 2 : 4. Triphenyl phosphite and tris(β-ethoxyethyl) phosphite drive the reaction towards the formation of compounds (LXX) and (LXXI), whose contents in the reaction products reach 87 and 83% respectively for an overall yield of the co-oligomers of 96%.[117] The temperature range 120–160 °C is optimal for the synthesis of compound (LXV); the maximum yields of the esters of vinyldocadienedioic acids are obtained in the range 40–80 °C depending on the structure of the activator. The most suitable solvents are toluene, benzene, and hexafluorobenzene.

The authors proposed the following co-oligomerisation mechanism:[116,117]



In the first stage butadiene and methyl acrylate are coordinated to the zerovalent nickel atom and form a coordination-unsaturated nickel σ,π-complex (LXXII) which can give rise to two 18-electron complexes (LXXIII) and (LXXIV) depending on the temperature. At an elevated temperature the complex (LXXIII), which gives rise to the ester of undeca-2,5,10-trienoic acid (LXV), is more stable. The insertion of methyl acrylate in the π-allyl–Ni bond at a lower temperature leads to the irreversible conversion of the complex (LXXIII) into the σ,σ-complex (LXXIV), which is transformed into the isomeric esters of vinyldodecadienedioic acids (LXX) and (LXXI). The formation of methyl 3,4-divinylcyclohexane-1-carboxylate (LXXVI) can be represented as a process proceeding via a stage involving the formation of the cyclic co-oligomer (LXXV) with its subsequent Cope rearrangement to the ester (LXXVI).

Numerous studies of the influence of various factors on the co-oligomerisation of buta-1,3-diene with methacrylic acid esters in the presence of nickel catalysts showed that three main products are formed: alkyl undeca-1,5,10-triene-2-carboxylate (LXXVII) and two isomeric alkyl esters of nonadeca-1,6,9,13,18-pentaene-10-carboxylic acid (XXVIII):[118]



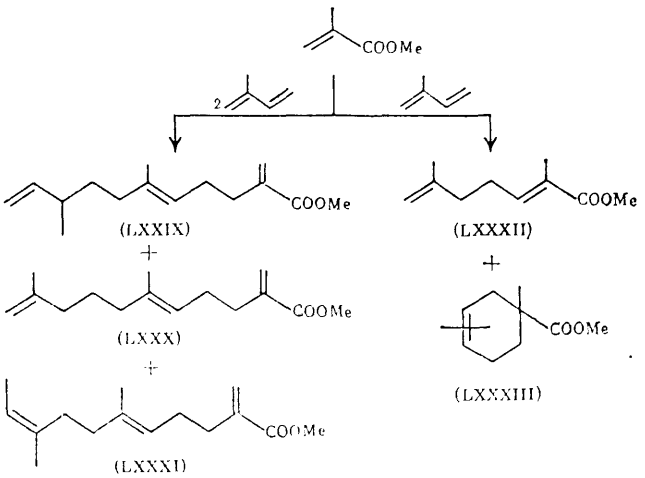
At 50 °C in the presence of a catalytic system comprising nickel acetylacetonate and triethylaluminium without activator, the yield of compound (LXXVII) reaches 24% and that of compound (LXXVIII) 54%. An increase of temperature promotes the formation of butadiene cyclisation products: cyclo-octa-1,5-diene and cyclododeca-1,5,9-triene.

One cannot say that all the data obtained reflect very clearly the influence of the structure of electron-donating ligands on the course of the co-oligomerisation of butadiene with alkyl methacrylates and the authors' conclusions can therefore be adopted only with some reservations. They believe that phosphines inhibit co-oligomerisation. Phosphites, particularly tris(o-biphenylyl) phosphite, promote the formation of cyclo-octa-1,5-diene (yield up to 60%). Phosphorous acid trimorpholide promotes the formation of compound (LXXVIII) in a good yield (69% after 120 h at 20 °C). In the presence of triphenylphosphines the above co-oligomer was isolated in a yield of 62% under analogous conditions. An appreciable yield of compound (LXXVIII) (79–87%) has been obtained in the presence of triphenylstibine. Like triphenylarsine, this ligand is more reactive and selective than triphenylphosphine (in the presence of triphenylarsine it was possible to achieve a 93% yield of methyl nonadeca-1,6,9,13,18-pentaene-10-carboxylate). Very high yields of compound (LXXVIII) (up to 88–92%) have been obtained using pyridine as the ligand. Its methyl, methoxy- and chloro-derivatives are less reactive.

The influence of the nature of nickel compounds on the results of the co-oligomerisation of buta-1,3-diene with methacrylates has been investigated.[118] In the presence of catalytic systems containing chloride ions co-oligomerisation does not occur. Satisfactory results have been obtained when nickel acetylacetonate was replaced by benzene-soluble nickel salts of lauric, palmitic, and certain other organic acids.

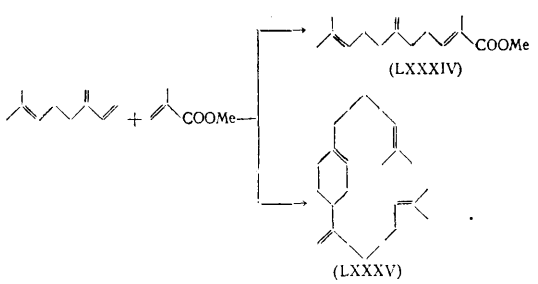
The co-oligomerisation of methyl methacrylate with isoprene and myrcene has been investigated in the presence of a homogeneous nickel catalyst (nickel acetylacetonate, reductant—ethoxydiethylaluminium).[119] The reaction with isoprene in the presence of this catalyst gives rise to three

main products: the methyl esters *trans*-6,9- and *trans*-6,10-dimethyl-2-methyleneundeca-5,10-dienoic acids (LXXIX) and (LXXX) and methyl *trans*, *cis*-6,9-dimethyl-2-methyleneundeca-5,9-dienoate (LXXXI) in proportions of 4 : 1 : 2 in an overall yield of 61% relative to the isoprene which has reacted.[119] Methyl *trans*-2,6-dimethylhepta-2,6-dienoate (LXXXII) and a cyclic adduct of isoprene and methyl methacrylate (LXXXIII) in an amount of 3% have also been found in the reaction products.



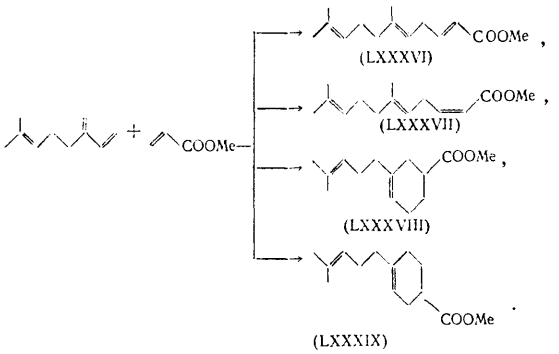
The co-oligomerisation was carried out at 66–76 °C for 8 h in toluene The degrees of conversion of isoprene and methyl methacrylate were 36 and 18% respectively. There was a considerable proportion (27.6%) of high-boiling products (residue after distillation).

Myrcene reacts with methyl methacrylate in the presence of nickel catalysts much more readily than isoprene. After only 1 h at 100 °C, the degree of its conversion reaches 95%, while that of methyl methacrylate reaches 20%. The main reaction products are methyl *trans*-2,10-dimethyl-6-methyleneundeca-2,9-dienoate (LXXXIV) (11.2%) and camphorene (LXXXV) (35.2%):



The co-oligomer of myrcene and methyl methacrylate with a molecular weight of 372 (27.6%) and high-boiling fractions of unknown composition (~23%) are formed as by-products.[119]

The codimerisation of myrcene with methyl acrylate has been been investigated in the presence of iron and cobalt complexes. It leads to the formation of linear codimers—methyl 6,10-dimethylundeca-2-*cis*(*trans*), 5-*trans*, 9-trienoates (LXXXVI) and (LXXXVII) and cyclic diene synthesis products (LXXXVIII) and (LXXXIX):[120]



Apart from these compounds, up to 8–10% of unidentified higher oligomers are formed in the reaction. The yields and proportions of the linear and cyclic codimers depend on the composition of the catalyst and the reaction conditions.

The maximum yield of the co-oligomerisation products is 75–80% relative to the myrcene which has reacted (the unreacted monomer is fully returned to the reactor); the degree of conversion of myrcene is up to 60–68%. The highest yield of linear codimers has been obtained in the presence of the catalytic system comprising $Fe(acac)_3$, PPh_3, and $AlEt_3$ in tetrahydrofuran. Cyclic esters are formed in this case in an amount of 17% of the total yield of the codimer. The content of cyclic products increases to 36–43% when $SbPh_3$, $P(C_6H_{11})_3$, and $Sb(OPh)_3$ are used as modifying agents. Cobalt compounds direct the reaction towards the formation of cyclic esters. Thus the addition of only 1% of cobalt acetylacetonate to the above catalytic system increases the yield of cyclic codimers to 50%. The complete replacement of iron acetylacetonate by cobalt acetylacetonate makes it possible to obtain the almost pure cyclic ester (LXXXVIII).

The solvents have an appreciable influence on the course of the reaction. On passing from ester solvents to aromatic hydrocarbons, the overall yield of codimers falls, but the fraction of cyclocodimerisation products and higher oligomers increases. A temperature of 50 °C is optimal; when it is reduced to 25 °C, the necessary reaction time increases sharply (from 10 to 100 h) and the yield of the codimers also remains low under these conditions.

The methyl esters of *cis*, *trans*, *trans*- and *trans*, *trans*, *trans*-undeca-2,5,9-trienoic acids in an overall yield up to 80% have been obtained on co-oligomerisation of methyl acrylate with octa-1,3,6-triene in the presence of systems consisting of iron or cobalt acetylacetonate, a phosphine modifying agent, and triethylaluminium.[121]

The possibility of the electrochemical cross-hydrodimerisation of 1,3-dienes, in particular butadiene, with ethyl acrylate and crotonate has been described.[122] The reaction proceeds via the recombination of intermediate radical-anions formed on the surface of the cathode at −15° or −20 °C. Dimethylformamide (DMF), anhydrous or containing 10% of water, or a 2:1 mixture of hexamethylphosphoramide and isopropyl alcohol with added tetrabutylammonium iodide, which increases the electrical conductivity of the electrolyte, have been used as solvents.

The composition and yield of the reaction products depend on the composition of the electrolyte. Thus in anhydrous DMF ethyl acrylate reacts with butadiene to form 1% of ethyl *trans*-hept-5-enoate (the product of the codimerisation of one molecule of buta-1,3-diene with one molecule of ethyl acrylate), 2.5% of diethyl *trans*-dec-5-enedioate (the product of the codimerisation of one molecule of buta-1,3-diene with two molecules of ethyl acrylate), and 7.5% of diethyl adipate

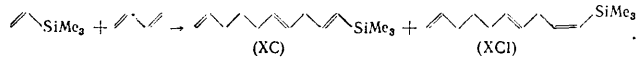
(the ethyl acrylate hydrodimerisation product). In aqueous DMF the yield of the ester of *trans*-dec-5-enedioic acid increases to 6.5%, that of diethyl adipate rises to 60%, while the ester of *trans*-hept-5-enoic acid was not detected in the reaction products.

Ethyl crotonate reacts with buta-1,3-diene in anhydrous DMF to form 8.7% of ethyl *trans*-3-methylhept-5-enoate and 5% of diethyl 3,4-dimethyladipate. In a mixture of the amide and the alcohol the yield of the 3,4-dimethyladipic ester increases to 68.7% and 7.9% of diethyl *trans*-3,8-dimethyldec-5-enedioate is formed instead of 3-methylhept-5-enoic acid ester.

3. Co-oligomerisation of Vinyl Derivatives of Silicon with Dienes and Trienes

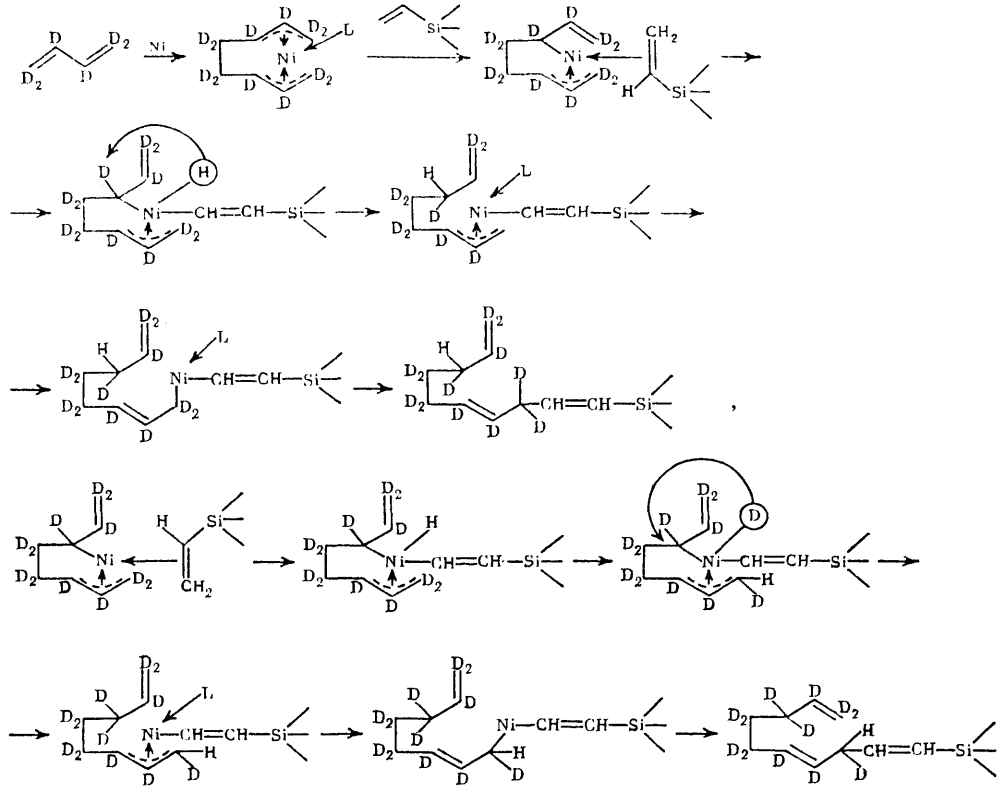
The linear co-oligomerisation of vinylsilanes with dienes and trienes is a new convenient procedure for the preparation of silicon-containing polyenes, which can serve as starting materials for the synthesis of a whole series of valuable products. These reactions have become the subject of study comparatively recently but extensive experimental data have already accumulated. These confirm that reactions of this kind can be carried out effectively.

The co-oligomerisation of butadiene with trimethylvinyl- and trimethoxyvinyl-silanes in the presence of the catalytic system consisting of nickel acetylacetonate, triphenylphosphine, and triethylaluminium has been investigated.[123–125] The co-oligomerisation with trimethylvinylsilane (100 °C, 8–10 h) results in a mixture of the silyldecatrienes (XC) and (XCI) in proportions of 1:1, which is obtained in a yield of 72%:

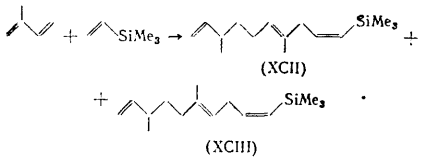


(XC) (XCI)

A change in the ratio of the initial monomers does not affect the composition of the reaction products. The formation of cyclic co-oligomers and homo-oligomers of the initial reactants has not been detected. Under analogous conditions, trimethoxyvinylsilane reacts with butadiene to form only one product—*cis*, *trans*-1-trimethoxysilyldeca-1,4,9-triene. The interaction of trimethylvinylsilane with deuterated butadiene has been studied and this has led to the following reaction mechanism:



Under the conditions described above, isoprene and trimethylvinylsilane react to form a mixture of isomeric silylated trienes (XCII) and (XCIII) in proportions of 3:1 and in a yield of 82%: [125]



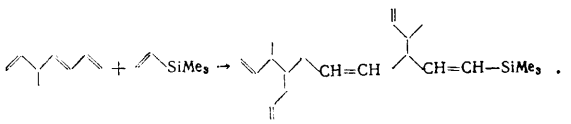
(XCII)

(XCIII)

Trimethoxyvinylsilane reacts with isoprene more selectively, giving rise to a 75% yield of pure *cis, trans*-1-trimethoxysilyl-5,8-dimethyldeca-1,4,9-triene. The only product of the co-oligomerisation of trimethylvinylsilane with piperylene is *trans, trans*-1-trimethylsilyl-3,7-dimethyldeca-1,4,9-triene (yield 70%):



Trimethylvinylsilane is more inert in the reaction with 3-methylhepta-1,4,6-triene. The yield of a mixture of the geometrical isomers of 1-trimethylsilyl-3-(1′-but-3′-enyl)-7-(1′-prop-3′-enyl)-8-methyldeca-1,4,9-trienes was only 30%:



The interaction of butadiene with trimethylvinylsilane in the presence of the catalytic system comprising nickel chloride, triphenylphosphine, and ethylaluminium sesquichloride($AlEt_{1.5}Cl_{1.5}$) is of the type of a telomerisation reaction and is completed by the formation of telomers having the general formula $H(CH_2CH{=}CHCH_2)_nC(=CH_2)SiMe_3$, where $n = 1-5$.

After 5 h at 60 °C, a mixture of hexadienyl- and decatrienyl- silanes is formed in an overall yield of 97% and with a degree of conversion of trimethylvinylsilane of 42%. [126] On increasing the temperature to 100 °C and the reaction time to 8 h, tetradecatetraenyl- and octadecapentaenyl-silanes are formed together with hexadienyl- and decatrienyl-silanes in an overall yield of 73% and with a degree of conversion of trimethylvinylsilane of 85%. Homo-oligomers of butadiene were not detected in the reaction products.

The co-oligomerisation of dichloromethylvinylsilane with butadiene in the presence of a catalyst consisting of tetrabutoxytitanium, triphenylphosphine, and triethylaluminium proceeds with formation of a mixture of *trans, trans*-hexa-1,4-dienyl- and *trans, trans, trans*-deca-1,4(5),8-trienyldichloromethylsilanes in proportions of 2:3. [127] The co-oligomerisation of butadiene with dimethoxymethylvinylsilane has been carried out successfully in the presence of the same titanium catalytic system, but in this case the formation of a mixture of decatrienylsilane isomers was established. [127] The use of nickel chloride, triphenylphosphine, and ethylaluminium sesquichloride made it possible to improve the selectivity of the reaction and to obtain the pure cotrimer—*trans, trans*-deca-1,4,9-trienyldimethoxymethylsilane. [127]

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Analysis of the data presented shows that catalytic systems permitting the oligomerisation reactions of olefins containing powerful electron-donating or electron-accepting substituents in direct proximity to the double bond have already been investigated. These processes resemble the oligomerisation reactions of olefins without functional groups which have been thoroughly studied. Further successful search for effective catalytic systems should therefore be directed towards the selection of the appropriate ligand environment around variable-valence metals, which will make it possible to achieve the required mode of oligomerisation of vinyl monomers ensuring the introduction into the final product of the necessary number of the functional groups present in the initial monomer. The highly effective electrochemical oligomerisation reactions of substituted olefins also merit the most careful attention.

REFERENCES

1. E.C.Coyner and W.S.Hillman, J.Amer.Chem.Soc., 1949, **71**, 324.
2. D.M.Gale, J.Org.Chem., 1970, **35**, 970.
3. M.Bolte and J.Lemaire, Compt.rend., 1979, **C288**, 403.
4. US P.3623966 (1971)
5. T.Saegusa, Y.Ito, H.Kinoshita, and S.Tomita, Bull.Chem.Soc.Japan, 1970, **43**, 877.
6. Japanese P.34410 (1971); Ref.Zhur.Khim., 1972, 13N53.
7. US P.3950370 (1976).
8. US P.3956358 (1976).
9. US P.415197 (1979).
10. US P.3920722 (1975).
11. Japanese P.8287 (1972); Ref.Zhur.Khim., 1973, 3N95.
12. M.M.Baizer and J.D.Anderson, J.Org.Chem., 1965, **30**, 1357.
13. French P.1366081 (1964).
14. B.P.1003656 (1965); Chem.Abs., 1966, **64**, 605.
15. French P.1388444 (1965); Chem.Abs., 1965, **63**, 504.
16. B.P.1224529 (1971); Chem.Abs., 1971, **74**, 124894.
17. US P.3652642 (1972).
18. French P.1411003 (1965); Chem.Abs., 1966, **64**, 1972.
19. US P.3225083 (1965); Chem.Abs., 1966, **64**, 19427.
20. J.D.McClure, J.Org.Chem., 1970, **35**, 3045.
21. US P.3562311 (1971); Chem.Abs., 1971, **74**, 88354.
22. Japanese P.35288 (1970); Ref.Zhur.Khim., 1972, 17N80.
23. US P.3567759 (1971).
24. US P.3538141 (1970).
25. B.P.1510707 (1978).
26. B.P.1514642 (1978).
27. BRD P.2752509 (1978); Chem.Abs., 1978, **89**, 108212.
28. B.P.1546807 (1979).
29. B.P.1547431 (1979).
30. B.P.1547432 (1979).
31. B.P.2027695 (1980).
32. N.Takashina and C.C.Price, J.Amer.Chem.Soc., 1962, **84**, 489.
33. B.P.1398089 (1975).
34. Japanese P.17212 (1971); Ref.Zhur.Khim., 1972, 2N94.
35. Japanese P.17217 (1971); Ref.Zhur.Khim., 1972, 2N89.
36. Japanese P.27729 (1971); Ref.Zhur.Khim., 1972, 8N219.
37. Japanese P.30815 (1971); Ref.Zhur.Khim., 1972, 11N71.

38. A.Misono, Y.Uchida, and M.Hidai, Bull.Chem. Soc.Japan, 1968, **41**, 396.
39. A.Misono, Y.Uchida, and H.Hidai, Chem.Comm., 1967, 357.
40. French P.1560994 (1969); Chem.Abs., 1970, **72**, 54816.
41. Japanese P.24585 (1969); Ref.Zhur.Khim., 1970, 13N120.
42. Japanese P.4048 (1970); Ref.Zhur.Khim., 1970, 24N89.
43. Japanese P.39330 (1971); Ref.Zhur.Khim., 1972, 20N76.
44. Japanese P.12450 (1979); Ref.Zhur.Khim., 1980, 3N89.
45. Japanese P.21369 (1971); Ref.Zhur.Khim., 1972, 5N104.
46. US P.3538133 (1970).
47. US P.3655724 (1972).
48. E.Billig, C.B.Strow, and R.L.Pruett, Chem. Communs., 1968, 1307.
49. French P.1564978 (1969); Chem.Abs., 1970, **72**, 66432.
50. D.J.Milner and R.Wheland, J.Organometal.Chem., 1978, **152**, 193.
51. Y.Masada and T.Yasui, Kogyo Kagaku Zasshi, 1971, **74**, 1714.
52. Japanese P.28488 (1974); Chem.Abs., 1975, **82**, 170115.
53. Japanese P.28489 (1974); Chem.Abs., 1975, **82**, 170119.
54. A.Misono, Y.Uchida, K.Tamai, and M.Hidai, Bull. Chem.Soc.Japan, 1967, **40**, 931.
55. J.D.Druliner and R.C.Blackstone, J.Organometal. Chem., 1982, **240**, 277.
56. V.A.Smirnov, Symposium "Vosstanovlenie Amal'gamami" (Reduction by Amalgams), Izd.Khimiya, Leningrad, 1970, p.210.
57. C.Van Eygen, Chim.et Ind., 1971, **104**, 71.
58. D.Danly, Symposium, "Elektrokhimiya Organicheskikh Soedinenii" (Electrochemistry of Organic Compounds) (Translated into Russian), Izd.Mir, Moscow, 1976, p.642.
59. F.Beck, "Electroorganische Chemie", Akademie-Verlag, Berlin, 1974, p.211.
60. A.P.Tomilov, Khim.Prom., 1978, 574.
61. T.Saegusa, Y.Ito, Sh.Tomita, and H.Kinoshita, J.Org.Chem., 1970, **35**, 670.
62. D.A.White and M.M.Baizer, J.Chem.Soc., Perkin Trans.I, 1973, 2230.
63. D.A.White, Synth.React.Inorg.Metal-org.Chem., 1977, **7**, 433.
64. J.Shabtai and E.Ney-Igner, J.Org.Chem., 1975, **40**, 1158.
65. USSR P.250130 (1970); Ref.Zhur.Khim., 1970, 21N57.
66. C.J.Albisetti, D.C.England, M.J.Hogsed, and R.M.Joyce, J.Amer.Chem.Soc., 1956, **78**, 472.
67. US P.3074999 (1963).
68. Japanese P.29646 (1970); Ref.Zhur.Khim., 1971, 16N90.
69. Japanese P.13369 (1971); Chem.Abs., 1971, **75**, 88135.
70. B.A.Feit, Europ.Polymer J., 1967, **3**, 523.
71. T.Alderson, E.L.Jenner, and R.V.Lindsey, J.Amer.Chem.Soc., 1965, **87**, 5638.
72. G.Barlow, M.J.Bryant, R.N.Haszeldine, and A.G.Mackie, J.Organomet.Chem., 1970, **21**, 215.
73. G.Oehme and H.Pracejus, J.prakt.Chem., 1980, **322**, 798.
74. H.Pracejus, H.G.Krause, and G.Oehme, Z.Chem., 1980, **20**, 24.
75. G.Oehme and H.Pracejus, Tetrahedron Letters, 1979, 343.
76. Hiroyoshi Kanai, J.Mol.Catal., 1981, **12**, 231.
77. A.P.Tomilov, S.G.Mairanovskii, M.Ya.Fyoshin, and V.A.Smirnov, in "Elektrokhimiya Organicheskikh Soedinenii" (Electrochemistry of Organic Compounds), Izd.Khimiya, Leningrad, 1968, p.170.
78. D.Tysse and M.Baizer, J.Org.Chem., 1974, **39**, 2823.
79. T.Saegusa, Y.Ito, Sh.Kabayashi, and S.Tomita, Chem.Comm., 1968, 273.
80. J.Shabtai and H.Pines, J.Org.Chem., 1965, **30**, 3854.
81. M.Ikeda and T.Hirano, Tetrahedron Letters, 1972, 4477.
82. M.Ikeda, T.Hirano, and T.Tsuruta, Tetrahedron, 1974, **30**, 2217.
83 M.Stickler and G.Meyerhoff, Makromol.Chem., 1980, **181**, 131.
84. I.Lingnau and M.Stickler, Europ.Polymer J., 1980, **16**, 785.
85. Y.Kazumi, Y.Kazuaki, and T.Yoshiyuki, Makromol Chem., 1981, **182**, 669.
86. G.H.Wagner, D.L.Bailey, A.N.Pines, M.L.Dunham, and D.B.McIntire, Ind.Eng.Chem., 1953, **45**, 367.
87. A.D.Petrov, Dokl.Akad.Nauk SSSR, 1954, **99**, 785.
88. W.K.Johnson and K.A.Pollart, J.Org.Chem., 1961, **26**, 4092.
89. V.P.Yur'jev, G.A.Gailyunas, F.G.Yusupova, G.V.Nurtdinova, E.S.Monakhova, and G.A.Tolstikov, J.Organometal.Chem., 1979, **169**, 19.
90. G.V.Nurtdinova, F.G.Yusupova, E.S.Monakhova, G.A.Gailyunas, V.N.Khvostenko, S.V.Rafikov, and V.P.Yur'ev, Dokl.Akad.Nauk SSSR, 1979, **249**, 114.
91. C.J.Albisetti, N.G.Fisher, M.J.Hogsed, and R.M.Joyce, J.Amer.Chem.Soc., 1956, **78**, 2637.
92. K.Alder and H.Brachel, Annalen, 1962, **651**, 141.
93. K.Kawamoto, A.Tatani, T.Imanaka, and S.Teranishi, Bull.Chem.Soc.Japan, 1971, **44**, 1239.
94. A.L.J.Beckwith and G.Moad, Austral.J.Chem., 1977, **30**, 2733.
95. B.B.Snider, J.Org.Chem., 1974, **39**, 255.
96. B.Akermark and A.Ljungqvist, J.Org.Chem., 1978, **43**, 4387.
97. B.B.Snider, D.J.Rodini, and J.Stranen, J.Amer. Chem.Soc., 1980, **102**, 5873.
98. B.B.Snider, Acc.Chem.Res., 1980, **13**, 426.
99. R.F.Childs, D.L.Mulholland, and A.Nixon, Canad.J.Chem., 1982, **60**, 801.
100. R.D.Sands, Synth.Comm., 1973, **3**, 81.
101. G.V.Nurtdinova, F.G.Yusupova, E.S.Monakhova, G.A.Gailyunas, V.D.Sheludyakov, and V.P.Yur'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 1416.
102. D.Wittenberg, Angew.Chem., 1963, **75**, 1124.
103. R.Müller, D.Wittenberg, H.Seibt, and E.Scharf, Angew.Chem., 1965, **77**, 318.
104. BRD P.1192640 (1966).
105. A.Misono, Y.Uchida, T.Saito, and K.Uchida, Bull.Chem.Soc.Japan, 1967, **40**, 1889.
106. G.A.Tolstikov, U.M.Dzhemilev, R.I.Khusnutdinov, and L.M.Zelenova, Zhur.Org.Khim., 1976, **12**, 315.
107. V.M.Akhmedov, M.A.Mardanov, and L.I.Zakharkin, Zhur.Org.Khim., 1972, **8**, 1779.
108. H.Singer, W.Umbach, and M.Dohr, Synthesis, 1971, 265.
109. G.A.Tolstikov, U.M.Dzhemilev, and R.I.Khusnutdinov, Zhur.Obshch.Khim., 1975, **45**, 1322.

110. U.M.Dzhemilev, R.I.Khusnutdinov, and G.A.Tolstikov, Zhur.Org.Khim., 1978, **14**, 243.
111. G.A.Tolstikov, U.M.Dzhemilev, R.I.Khusnutdinov, and S.R.Rafikov, Dokl.Akad.Nauk SSSR, 1975, **224**, 609.
112. G.A.Tolstikov, U.M.Dzhemilev, and R.I.Khusnutdinov, Zhur.Org.Khim., 1979, **15**, 694.
113. USSR P.583121 (1978); Ref.Zhur.Khim., 1978, 21N48.
114. French P.1433409 (1965); Chem.Abs., 1967, **66**, 37449.
115. G.I.Myagkova, A.V.Novozhilov, V.P.Nechiporenko, A.B.Prokhorov, and R.P.Evstigneeva, Zhur. Org.Khim., 1972, **8**, 1795.
116. O.S.Vostrikova, U.M.Dzhemilev, G.A.Tolstikov, and L.M.Zelenova, Izv.Akad.Nauk SSSR, Ser. Khim., 1975, **9**, 2018.
117. U.M.Dzhemilev, O.S.Vostrikova, and G.A.Tolstikov, Neftekhimiya, 1976, **16**, 439.
118. H.Singer, W.Umbach, and M.Dohr, Synthesis, 1972, 42.
119. E.Klein, F.Thomel, H.Struwe, P.Heimbach, and H.Schenkluhn, Annalen, 1976, 352.
120. G.A.Tolstikov, U.M.Dzhemilev, and R.I.Khusnutdinov, Izv.Akad.Nauk SSSR, Ser.Khim., 1975, 1562.
121. R.I.Khusnutdinov and U.M.Dzhemilev, Symposium, "Khimiya Vysokomolekulyarnykh Soedinenii i Neftekhimiya" (The Chemistry of Macromolecular Compounds and Petrochemistry), Izd.Bashkir, Fil.Akad.Nauk SSSR, Ufa, 1975, p.53.
122. H.G.Thomas and F.Thönnessen, Chem.Ber., 1979, **112**, 2786.
123. F.G.Yusupova, G.A.Gailyunas, I.I.Furlei, A.A.Panasenko, V.D.Sheludyakov, G.A.Tolstikov, and V.P.Yur'ev, Izv.Akad.Nauk SSSR, Ser.Khim., 1979, 599.
124. F.G.Yusupova, G.A.Gailyunas, J.J.Furley, A.A.Panasenko, V.D.Sheludyakov, G.A.Tolstikov, and V.P.Yurjev, J.Organometal.Chem., 1978, **155**, 15.
125. F.G.Yusupova, G.V.Nurtdinova, G.A.Gailyunas, G.A.Tolstikov, S.R.Rafikov, and V.P.Yur'ev, Dokl.Akad.Nauk SSSR, 1978, **239**, 1385.
126. G.A.Gailyunas, G.V.Nurtdinova, F.G.Yusupova, L.M.Khalilov, V.K.Mavrodiev, S.R.Rafikov, and V.P.Yurjev, J.Organometal.Chem., 1981, **209**, 139.
127. G.V.Nurtdinova, F.G.Yusupova, E.S.Monakhova, V.G.Lakhtin, G.A.Gailyunas, and V.P.Yur'ev, Zhur.Obshch.Khim., 1980, **50**, 704.

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