Translated from *Uspekhi Khimii*, 44, 1217 - 1235 (1975) U.D.C. 547.212;547.311.2;541.49

Alkylation and Arylation of Unsaturated Compounds with the Aid of Transition Metal Complexes

L.G.Volkova, I.Ya.Levitin, and M.E.Vol'pin

Methods for the alkylation and arylation of unsaturated compounds with the aid of Group VIII metal complexes are examined and both the preparative aspects and the mechanism of the reactions involving the introduction of various organic groups into olefins are discussed.
The bibliography includes 77 references.

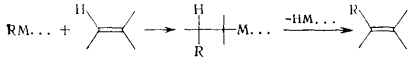
CONTENTS

I. Introduction 552
II. Alkylation and arylation of olefins by organic transition metal σ derivatives obtained by double decomposition reactions between Group VIII metal salts and organometallic compounds 552
III. Alkylation and arylation of olefins by organic halogeno-derivatives in the presence of Group VIII metal compounds 557
IV. Arylation of olefins by aromatic compounds in the presence of transition metal salts 558

I. INTRODUCTION

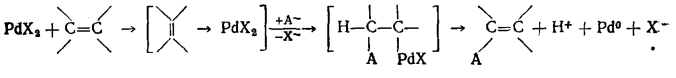
In the chemistry of olefins reactions occurring under the influence of transition metal compounds have been acquiring increasing importance. Important industrial processes such as polymerisation of olefins at low temperatures and pressures, direct oxidation of propene to acrolein, the oxidation of propene and ammonia to acrylonitrile, the oxidation of olefins in the presence of vanadium salts with formation of carbonyl compounds and vinyl esters of carboxylic acids, and the hydroformylation and disproportionation of olefins were introduced in the course of the last two decades.

Significant advances have also been achieved in the development of methods for the consecutive growth of the carbon chain in unsaturated compounds. The classical Meerwein reaction[1]—the arylation of olefins by diazonium salts in the presence of copper compounds—is of limited importance, since it makes it possible to introduce only an aromatic residue into the unsaturated molecule. The use of Group VIII metal complexes has given rise to good prospects for the introduction of organic groups into olefins. Their application is based on the capacity of certain organometallic σ derivatives of these elements, particularly those of palladium, to add to the double bond and on the instability of the addition products with respect to β-elimination:



Although the oligomerisation, disproportionation, and hydroformylation of olefins should be formally included in the type of processes under consideration, we shall not discuss them here, since an extensive literature has been devoted to each of these reactions. The oligomerisation and cyclooligomerisation reactions[2] are particularly characteristic of compounds with the C≡C triple bond in the presence of Group VIII metal complexes, while the growth of the carbon chain in acetylene derivatives is achieved more readily by the methods which have been thoroughly developed in organic chemistry. For this reason, attention will be concentrated in the present review on the introduction of alkyl and aryl groups into compounds with a C=C double bond, which is of preparative interest.

The interaction of olefins with transition metal complexes is known to involve in many instances the ready formation of π complexes. As a result of the changes in the electronic structure of the unsaturated ligand, the reactivity of the double bond in many π complexes in relation to nucleophilic reagents increases compared with the free olefin. Nucleophilic addition to π complexes has been comparatively thoroughly investigated in the chemistry of palladium. If there are no factors favouring the stabilisation of metal–carbon σ bond in the resulting compound (for example the influence of other ligands or of chelate formation), the hydride is eliminated and the overall process reduces to the substitution of the vinyl hydrogen:

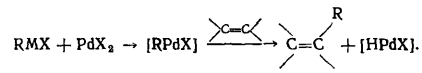


The mechanism of such reactions has been thoroughly studied by Moiseev in the oxidation of olefins by palladium(II) compounds[3]. It was shown that the intermediates in this reaction are labile organopalladium σ compounds obtained as a result of a rearrangement of the palladium complex containing the olefin, joined by a π bond, and a solvent molecule[4-6]. These fundamental stages are apparently characteristic of the majority of the reactions discussed in the present review.

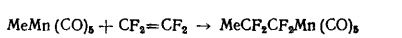
II. ALKYLATION AND ARYLATION OF OLEFINS BY ORGANIC TRANSITION METAL σ DERIVATIVES OBTAINED BY DOUBLE DECOMPOSITION REACTIONS BETWEEN GROUP VIII METAL SALTS AND ORGANOMETALLIC COMPOUNDS

The possibility, in principle, of the formation of labile organopalladium σ complexes in double decomposition reactions of organomercury compounds with palladium salts was demonstrated by Moiseev in 1960[4]. Ways of employing such complexes in organic syntheses were discovered in 1968 by Heck[7]. He succeeded in synthesising a wide range of alkylated and arylated olefins by

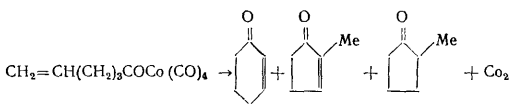
allowing the olefin to react jointly with a transition metal salt and an organic derivative of a non-transition metal[7-12]:



It is noteworthy that, even before these investigations by Heck, instances were known where the interaction of alkyl σ complexes of transition metals with olefins resulted in the formation of a new carbon–carbon bond, namely the addition of methylmanganese pentacarbonyl to tetrafluoroethylene with formation of a new organometallic complex[13]:



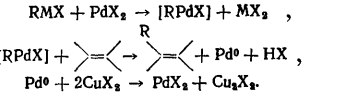
and the cyclisation of the organic ligand of hex-5-enoylcobalt tetracarbonyl, which resulted in a mixture of cyclohexenone, 2-methylcyclopentenone, and 2-methylcyclopentanone[14]:



A characteristic feature of the new stage in the wide-scale application of transition metal compounds for the alkylation and arylation of olefins was the use of stable organometallic compounds of non-transition metals as the source of organic groups. Heck and other investigators showed[7,15-20] that such donors or organic groups may be derivatives of lithium, magnesium, thallium, mercury, tin, and lead. However, these organometallic compounds are either sensitive to air and moisture (organolithium and organomagnesium compounds) or are highly toxic (organic derivatives of mercury, tin, thallium, and lead), so that their use in many cases involves significant difficulties. The recently discovered possibility of using organosilicon compounds—alkyl- and aryl-silanes, which are stable, non-toxic, and relatively readily available—as sources of alkyl and aryl groups in these reactions[21,22] is therefore of interest. Symmetrical organic derivatives Ar_2E, where E = P, As, Sb, or Bi, can also be used for arylation[23,24]. It has been shown that stable alkyl and aryl σ complexes of cobalt, rhodium, and iron with chelating ligands RM(Chel), where R = Me, Ph, or $PhCH_2$ and Chel = bis(dimethylglyoximate), bis(salicylidenato)ethylenediamine, and corrin and phthalocyanine ligands[25,27].

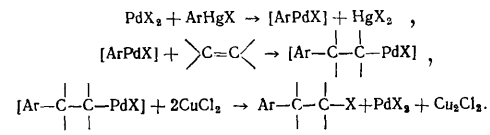
In most cases the above reactions occur at room temperature in various polar solvents, such as methanol, acetonitrile, acetic acid, and tetrahydrofuran and lead to the formation of substituted olefins in yields which are nearly quantitative in many cases. In arylation with the aid of compounds of Group VA elements more severe conditions are required (refluxing in an acetic acid–dioxan mixture)[24], probably in order to suppress the coordination of palladium to these compounds via a heteroatom.

The most active "transferring" agents for organic groups in these reactions are palladium compounds, the rhodium, ruthenium, and nickel complexes being less active[7]. Upon reaction, the transition metals acquire the zero oxidation state. The use of suitable reoxidising agents, such as copper(II) chloride, and iron and mercury salts, permits their regeneration and thus makes the reaction catalytic[7]:



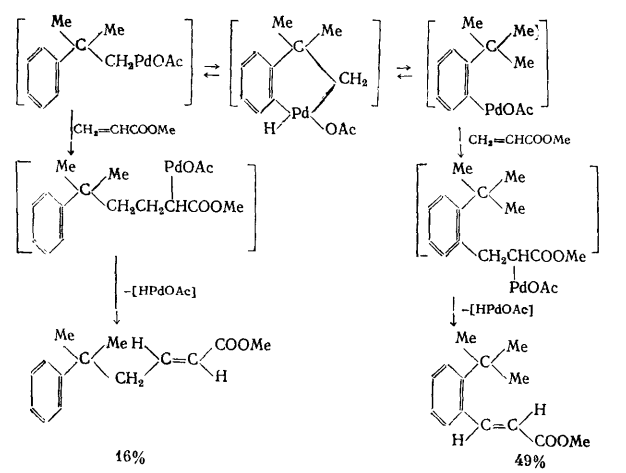
Copper(II) chloride can be regenerated from copper(I) chloride with the aid of atmospheric oxygen and hydrogen chloride.

In those cases where the concentration of the copper salt in solution exceeds 0.5 M halogeno-derivatives are also formed and the halogenoethylation reaction can become the main one[10]. For example, the reaction of phenylmercury chloride with ethylene in the presence of catalytic amounts of $PdCl_2$ and $CuCl_2$ at a concentration of 2 M results in the formation of phenylethyl chloride in 76% yield:

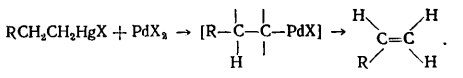


This reaction is itself also very useful for synthetic organic chemistry, because there is no other way of adding, in a single stage, a 2-halogenoethyl group to an olefin.

Alkylation of unsaturated compounds by organopalladium σ complexes makes it possible to introduce into olefins alkyl groups without a β-hydrogen atom, such as the methyl, carboxyalkyl[7], benzyl, and neopentyl[28] groups. From the standpoint of synthesis, the transfer of the neopentyl group as a method for the introduction of a quaternary carbon atom into an unsaturated molecule is of special interest. The transfer of another group fully substituted in the β-position—2-methyl-2-phenylpropyl—is accompanied by an interesting rearrangement, probably in the stage involving the formation of the organopalladium σ compound, so that the normal product is accompanied by an olefin with the *o*-(t-butyl)-phenyl substituent at the double bond:

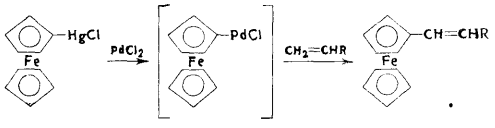


The attempts to transfer groups containing hydrogen in the β-position were unsuccessful: the olefin corresponding to β-elimination from the alkyl group was obtained instead of the alkylated products[7]:



Like alkyl groups without β-hydrogen, aryl groups with various substituents can be introduced into unsaturated molecules with the aid of transition metals[7]. Under these conditions, powerful electron-donating groups such as the methoxy-, hydroxy-, and diethylamino-groups in the *ortho*- and *para*-positions, lower the yield of the arylated olefins; substituents with a marked capacity for coordination to metals, for example the amino-group, hinder still more the reaction or preclude it altogether.

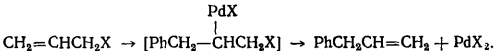
Subsequently arylation by a non-benzenoid aromatic system was achieved—the ferrocenyl residue was introduced into olefins[29]:



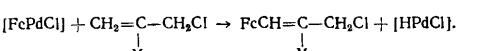
The nature of the olefin also plays a significant role in the above reaction. In particular the arylation of olefins with the normal structure and a short chain proceeds more readily and with higher yields. The relative rates of arylation decrease in the following sequence[7]:

$$\underset{14\,000}{CH_2=CH_2} > \underset{970}{CH_2=CHCOOMe} > \underset{220}{MeCH=CH_2} > \underset{42}{PhCH=CH_2} > \underset{1}{MeCPh=CH_2}.$$

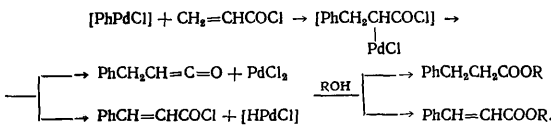
The arylation of olefins with functional groups has also been achieved. If a complex containing in the β-position relative to the metal a group tending to form an anion is formed in the interaction between the substituted olefin and the organopalladium compound, the decomposition of this complex can proceed with elimination of the corresponding anion instead of the hydride. For example, in the arylation of allyl halides the intermediate organopalladium compound decomposes exclusively with the elimination of the chloride ion[9]:



Aryl groups with various substituents (the nitro-group and ether and aldehyde groups) were introduced in this way into the allyl position. On the other hand, when the ferrocenyl group is introduced into allyl chloride, palladium hydride is split off and not the chloride[27]:

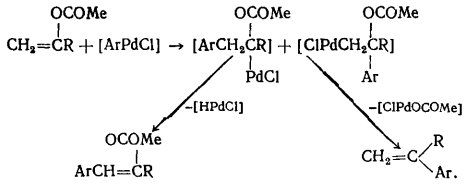


Arylation of the chlorides of αβ-unsaturated acids in the presence of $PdCl_2$ led to the formation of a mixture of various products[30]:

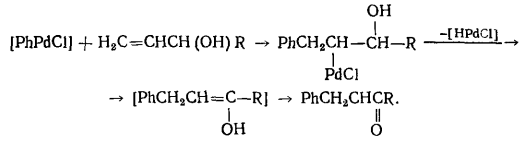


Depending on the pathway in the decomposition of the organopalladium complex, with elimination of $PdCl_2$ or [HPdCl], esters of β-phenylpropionic or substituted cinnamic acids are formed in the subsequent alcoholysis. However, the yields of both are low, of the order of 10 to 16%, so that the reaction in this form has no preparative interest.

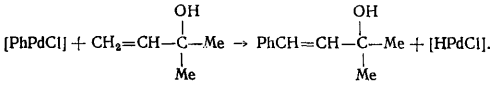
The reaction of enol ethers and esters with arylpalladium salts, obtained *in situ*, gives rise to various products, depending on the mode of addition of the organopalladium compound (see p. 556) and on the nature of the species eliminated[10]:



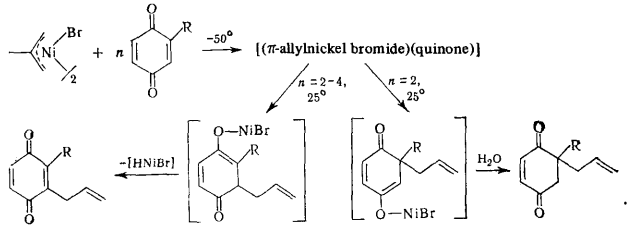
In certain cases the arylation reactions of substituted olefins are accompanied by rearrangements. For example, phenylation of primary or secondary allyl alcohols leads to 3-aryl-substituted aldehydes and ketones, probably via the corresponding enols[8]:



Tertiary ally alcohols react normally:



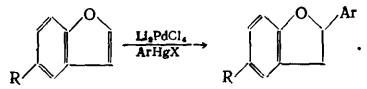
Examples of the introduction of substituents into benzo- and naphtho-quinones with the aid of Group VIII metal complexes are now known. The reaction of π-allylnickel bromides with *p*-quinones, discovered by Hegedus et al.[31], which makes it possible to introduce an allyl substituent into the quinones, is of great interest. The synthesis is carried out in polar solvents, [tetrahydrofuran (THF), dimethylformamide (DMF)] in two stages. Mixed allyl–quinone π complexes of nickel are formed at a low temperature (−50°C), while the second stage takes place at room temperature. In particular, coenzyme Q_1 and 1-plastoquinone were obtained by this method in 40 and 30% yields respectively. The authors represent this reaction by the following general scheme:



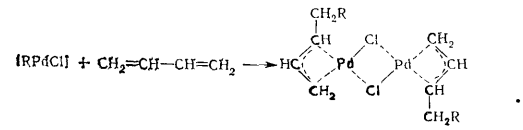
Thus the reaction with a monosubstituted *p*-benzoquinone results in the formation of a mixture of isomeric allylquinones and, for a comparatively small quinone: nickel complex reactant ratio cyclohexenedione derivatives are also formed. In the first two stages 1,4-addition probably takes place. However, the third stage suggested by the authors—the elimination of the hydride—appears unlikely; the oxidation of the cyclohexadienone derivative by an excess of the initial quinone is more probable.

Kim et al. [32] found that *p*-quinones can be methylated by methylpalladium complexes obtained *in situ* from a palladium salt and a methylcobalt chelate. In the methylation of *p*-benzoquinone the yield is very low (4%); but in the case of 1,4-naphthoquinone it is much higher (30–40%). The palladium salt can be replaced by a nickel salt, although the yield is then appreciably reduced.

The unsaturated systems capable of being arylated include certain heterocyclic compounds [33]. The interaction of benzofuran with intermediate arylpalladium chloride leads to the formation of 2-arylbenzofuran derivatives:

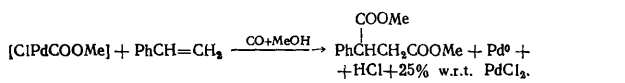


Conjugated dienes such as butadiene and cyclohexa-1,3-diene react with alkyl-, aryl-, and ferrocenyl-palladium compounds obtained *in situ*, with formation of stable allyl π complexes [12, 34]:

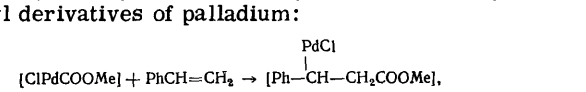


Methyl 5-ferrocenylsorbate was obtained directly from methyl sorbate and ferrocenylpalladium chloride, evidently also via an allyl π intermediate.

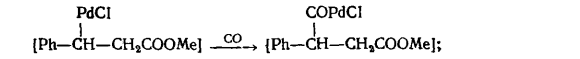
Reactions involving the insertion of simple molecules, particularly CO, in the palladium–carbon bond in the intermediate organopalladium σ compounds give rise to extensive synthetic possibilities. We shall quote several examples of reactions of this kind. Thus Heck discovered the reaction involving the addition of two methoxycarbonyl groups to multiple bonds [35]. When olefinic and acetylenic hydrocarbons are acted upon by methoxycarbonyl derivatives of palladium [obtained directly from $PdCl_2$, methanol, and CO or by the double decomposition reaction of palladium(II) with the corresponding organomercury compound], dialkoxycarbonyl derivatives are formed:



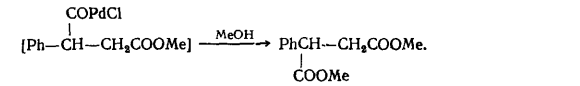
The olefin probably reacts initially with the methoxycarbonyl derivatives of palladium:



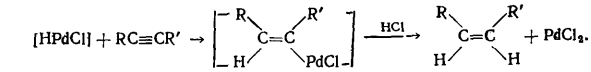
and then a CO molecule is inserted in the new palladium–carbon bond:



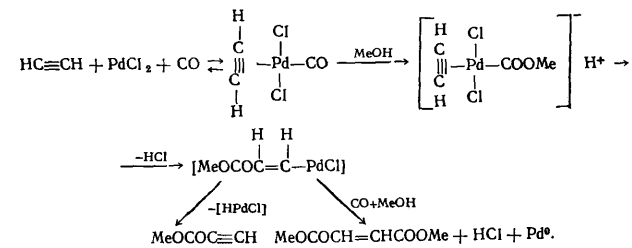
after this, the organometallic compound undergoes alcoholysis:



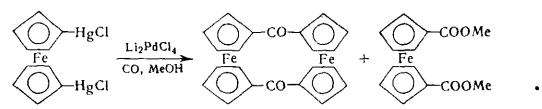
In the reactions with acetylene the yields of the products exceed the stoichiometric values (up to 200%), which can be accounted for by the regeneration of the palladium(II) compound as a result of the oxidation of zero-valent palladium by acetylene:



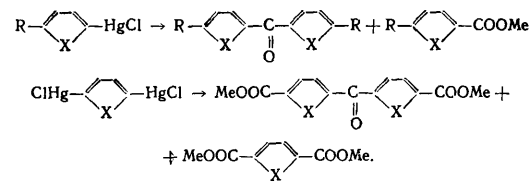
Overall, the reaction with acetylenes can be represented as follows:



The carbonylation of 1,1′-bis(chloromercury)ferrocene with the aid of a palladium salt in methanol at 70°C and a CO pressure of 50 atm led to the synthesis of 1,1-ferrocenophane-1,12-dione [36]:



The carbonylation of organomercury derivatives of the furan and thiophen series was achieved by means of the same scheme [37]:

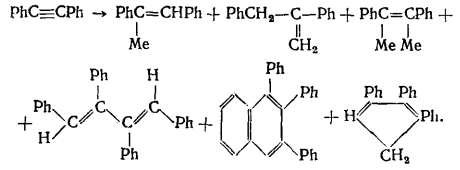


Generalising the reactions discussed in the present section, in which olefins are alkylated and arylated by organic σ derivatives of transition metals, obtained by double decomposition reactions of organic derivatives of non-transition metals with Group VIII metal salts, one may conclude that this procedure has great possibilities for the synthesis of a wide variety of derivatives of unsaturated compounds.

In all the reactions examined the intermediate formation of transition metal σ complexes is postulated, but these complexes cannot be isolated in view of their high kinetic lability. There exists only indirect evidence for their formation. In particular, in a study of the alkylation of olefins by organic derivatives of chelate complexes of cobalt in the presence of palladium compounds it was possible to isolate bis-π-allylpalladium chloride, formed as a result of the double decomposition reaction between the allyl derivative of the cobalt chelate and palladium(II). [26] Presumably the allyl π complex is formed on rearrangement of the intermediate π-allylpalladium chloride.

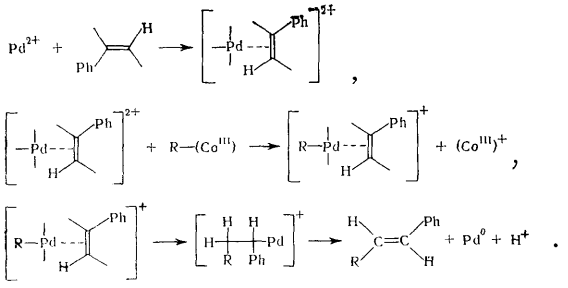
The reaction of the methyl σ complex of rhodium $MeRh(PPh_3)_3$ with diphenylacetylene can serve as an example of the alkylation of an unsaturated compound by a more stable organic σ derivative of a transition metal.

It results in the formation of the same products as in the alkylation of tolane by MeMgBr in the presence of $RhBr_3 \cdot 3H_2O$, $Rh(PPh_3)_3Br$, or $(PhCN)_2Pd$ [15,16]:



The main product is α-methylstilbene, with the additional formation of isomerisation, dimethylation hydrogenation, and cyclisation products.

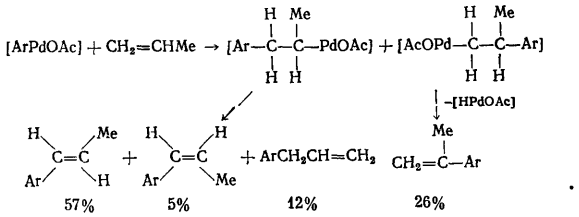
The mechanism of the intermediate formation of organopalladium σ compounds, has been studied in relation to the interaction of palladium complexes with organic derivatives of chelate Group VIII metal complexes of olefins, where this stage is apparently rate-limiting[38]. It was shown that the dealkylation of methylcobalamine by lithium chloropalladate in the presence of styrene proceeds approximately fifty times faster than in its absence. Evidently the stage involving the transfer of the organic ligand from cobalt to palladium precedes the formation of the π complex of palladium with the olefin. The next stage is apparently the exchange proper of the organic group between the organometallic compound and the olefinic π complex of palladium, the influence of the olefinic ligand in the π complex promoting the labilisation of the Pd–Cl bond in the *trans*-position relative to it:



The observed electronic effects in the reactions considered correspond to the usual rules governing electrophilic substitution at a metal atom.

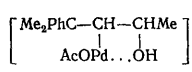
Later a study was published in which the kinetics of the transfer of the methyl group from methylcobalamine to palladium(II) were investigated in the absence of any organic substrate[39]. The reaction products were aquocobalamine, metallic palladium, and methyl chloride. In discussing the reaction mechanism, the authors also suggest the intermediate formation of a methylpalladium σ complex as a result of electrophilic attack by Pd^{2+} on the carbon atom linked to cobalt.

In studies of the arylation and alkoxycarbonylation of olefins by organopalladium compounds factors on which the mode of addition of the organic group to the olefin depends were determined[40,41]. It was found that in the main the reaction mechanism is determined by steric factors, namely the large organic group adds preferentially to the less substituted carbon atom involved in the double bond and palladium therefore adds to the more substituted carbon atom. When the steric and electronic factors act in the same direction, the reaction becomes fairly selective. For example, in the methylation of styrene by "methylpalladium acetate" 95% of trans-β-methylstyrene, about 3% of the *cis*-isomer, and only 2% of α-methylstyrene is obtained. In the arylation of propene the steric and electronic factors act in opposition. The principal mode of substitution is in this case determined by steric effects:

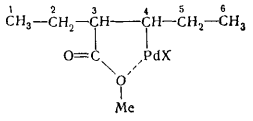


However, the ratio of the yields of products shows that the electronic effects are nevertheless manifested quite distinctly.

In cases where there is a possibility of the formation of a chelate intermediate, this implies a significant influence on the mode of the reactions under consideration. This effect is observed in the arylation reactions of allyl alcohols which we have already discussed[8]. The addition of the phenyl group to such alcohols takes place preferentially at the terminal carbon atom involved in the double bond of the alcohol. This cannot be accounted for either by electronic or steric effects. The mode of addition is in this case probably determined by the possibility of the formation of the four-membered ring

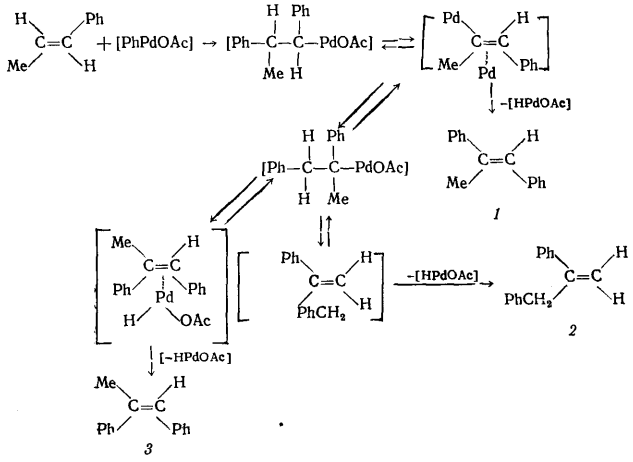


in the intermediate organopalladium compound. The same effect is manifested in the methoxycarbonylation of cyclic olefins and olefins with an inner double bond, leading to preferential substitution in the allyl position. For example, in the methoxycarbonylation of *trans*-hex-3-ene the following chelate intermediate may be formed:



Evidently the *cis*-elimination of the hydride from the 3-position in this complex cannot occur.

Identification of the products obtained in the reaction of "phenylpalladium acetate" with *trans*-1-phenylprop-1-ene yielded information about the stereochemistry of the reaction:

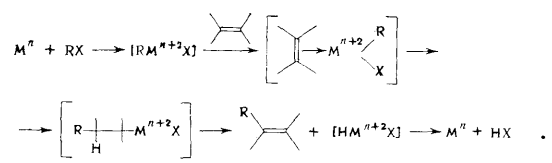


The reaction results in the formation of a mixture of olefins with a nearly quantitative overall yield. The principal product is *trans*-1,2-diphenylprop-1-ene (*1*) (98% yield) with the additional formation of 2,3-diphenylprop-1-ene (*2*) (0.5% yield) and only traces of *cis*-1,2-diphenylprop-1-ene (*3*). The formation of the *trans*-isomer corresponds to the mechanism involving the *cis*-addition of [PhPdOAc] to propenylbenzene with the *cis*-elimination of [HPdOAc]. The preferential formation of *trans*-1,2-diphenylprop-1-ene might be accounted for also with the aid of the *trans*-addition–*trans*-elimination mechanism. However, this appears unlikely[3,40,41], since the reaction should then proceed intermolecularly and not in the inner coordination sphere of palladium.

The selectivity of the substitution of the vinyl hydrogen atom in olefins is significantly influenced by the nature of the anion in the initial palladium complex. The selectivity increases on replacement of the chloride ion by the acetate ion[40,42,43]. It was established that the use of chlorides induces the isomerisation of olefins (both the migration of the double bond and *cis–trans* isomerisation). This can probably be explained by the greater stability of the complex [HPdCl] compared with [HPdOAc]. There is probably sufficient time for the hydride complex [HPdCl] to add several times to the double bond and to be split off before its decomposition into zero-valent palladium and HX. Such partial reversibility of the elimination of the hydride leads to a decrease of selectivity, namely to an increase of the yield of the thermodynamically more stable isomer.

III. ALKYLATION AND ARYLATION OF OLEFINS BY ORGANIC HALOGENO-DERIVATIVES IN THE PRESENCE OF GROUP VIII METAL COMPOUNDS

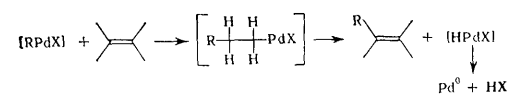
The studies carried out in recent years have shown that not only organometallic compounds but also purely organic reagents, in particular organic halogeno-derivatives, can serve as donors of the alkyl and aryl groups in olefin substitution reactions carried out with the aid of transition metal compounds. The possibility, in principle, of achieving such reactions is based on the ability of metals in a low oxidation state to enter into oxidative addition reactions and on the ability of the resulting complex to interact with the olefin:



Catalytic reactions involving the substitution of the vinyl hydrogen atom of olefins by aryl, benzyl, and styryl halides with the aid of palladium have now been achieved[44–46]. These reactions are carried out in methanol[44,45] or without a solvent[46] at 100°C and atmospheric pressure. The active catalysts are zero-valent palladium and palladium(II) salts. In the latter case the reaction probably begins with the reduction of palladium(II) to zero-valent palladium under the influence of the olefin or methanol. This is followed by the oxidative addition of the organic halogeno-derivative to the zero-valent palladium. The observed reaction rate is determined by the rate of this stage. The reactivity of aryl halides varies in the sequence PhI > PhBr ≫ PhCl, which corresponds to the change in the bond energy between carbon and halogen. The interaction results in the formation of an organopalladium σ complex:

$$Pd^0 + RX \rightarrow [RPd^{II}X].$$

The subsequent interaction of this complex with the olefin leads to the formation of a substituted olefin and the unstable palladium hydride:



The zero-valent palladium is involved in the next reaction cycle.

The accumulation of HX in the reaction medium has an inhibiting effect on the reaction. The point is that the σ complex [RPdX] is unstable in relation to the action of acids; it can be split into RH and PdX_2. Furthermore, an acid medium promotes the hydrogenation of olefins. For this reason, various bases are used to bind HX: potassium acetate and benzoate, pyridine, triethylamine[44,45], and tri-n-butylamine[46].

These reactions are applicable to various substituted olefins containing nitro-, methoxy-, and methoxycarbonyl groups. In the case of olefins containing a methylene group next to the double bond the yields of the reaction products are relatively low[46]. This can be explained by the formation of allyl π complexes of such olefins with the catalysts.

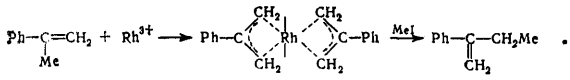
Despite their advantages over arylation, benzylation, and styrylation by organometallic derivatives these reactions also suffer from certain limitations, namely the reaction products are usually a mixture of geometrical isomers, the isomerisation taking place intramolecularly, possibly via a π complex of palladium hydride with the olefin. This is supported by the finding that none of the initial olefins isomerises under the reaction conditions. Since the reaction proceeds at an elevated temperature, the migration of the double bond becomes appreciable. Furthermore, one cannot employ in the reaction starting materials sensitive to the action of bases. This probably explains the failure of the attempts to alkylate olefins by alkyl halides under these conditions.

Olefins were successfuly methylated by methyl iodide in another system using rhodium compounds[47]. The methylation of styrene, linear terminal olefins, and cyclohexene was achieved under the joint action of methyl iodide or chloride or tetramethylammonium iodide and rhodium trichloride in the presence of a reducing agent. The reducing agents used are primary and secondary alcohols and also bivalent tin. Weak bases such as DMF and acetronitrile are used to bind HX in this reaction. Reactions are carried out at 100–160°C using an excess of the olefin. The methylated olefins are formed in stoichiometric yields.

The active species in the reaction is probably a complex of rhodium(I), which is involved in the oxidative addition of MeI. However, this complex is unstable and is partly converted into zero-valent rhodium under the reaction conditions, which was found to be incapable of transferring the organic group to the olefin. This factor complicates the catalytic process.

Together with monomethylated olefins, the formation of small amounts of doubly methylated olefins has been observed in a number of instances. This can be explained

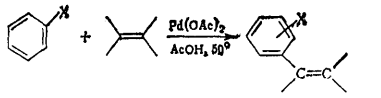
by the subsequent methylation of the allyl π complex of rhodium with the monosubstituted olefin:



IV. ARYLATION OF OLEFINS BY AROMATIC COMPOUNDS IN THE PRESENCE OF TRANSITION METAL SALTS

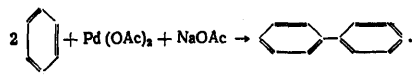
The communications of Fujiwara and coworkers [42, 48, 49] concerning the reactions of olefins with benzene derivatives in the presence of palladium(II) salts, which appeared in 1967, initiated a whole series of investigations on the synthesis of substituted olefins using a wide variety of aromatic compounds as arylating agents.

The interaction of benzene derivatives, an olefin, and palladium acetate results in the formation of aryl-substituted olefins [42, 48, 47]:



The reactions are carried out with equivalent amounts of the olefin and palladium(II) acetate in a large excess of the aromatic compound in the presence of acetic acid. The reaction does not proceed without the acid. The yield of the arylation products varies from 10 to 90% and metallic palladium is produced. When silver and copper acetates are added to the reaction mixture [50] or the reaction is performed under oxygen pressure [51, 52], it can be made catalytic as a result of the regeneration of palladium(II).

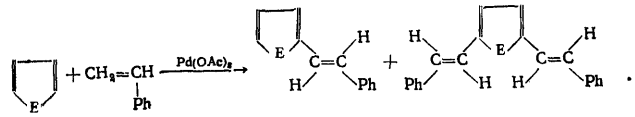
It is noteworthy that the arylation of olefins is accompanied by the dimerisation of the aromatic radicals. The addition of nucleophilic reagents causes the reaction to be of the preformation type and permits its employment for the synthesis of biaryl derivatives [52-61]:



Intramolecular aromatic substitution can also be achieved with the acid of palladium(II). [62] Thus the reaction of the olefins $PhR_2C-CH=CH_2$ (R = Ph or Me) with palladium(II) acetate in acetic acid at 80°C results in the formation of the corresponding 1,1-disubstituted indenes:



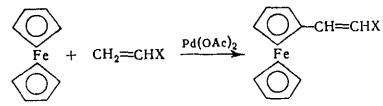
Together with benzene derivatives, other compounds with aromatic properties such as heterocycles [33, 63] and ferrocene [64-66] proved to be active arylating agents. It has been shown that furan, thiophen, selenophen, *N*-methylpyrrole, and *trans*-2-styrylfuran arylate olefins with high yields, disubstituted derivatives being formed together with monoarylated derivatives:



E = O, S, Se.

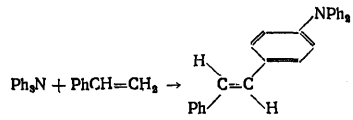
The authors believe that the reaction proceeds in two stages: monosubstituted products are formed in the first stage and further alkenylation takes place in the second stage. This is not observed in the reaction of benzenoid aromatic compounds with olefins [48]. Substitution in heterocycles takes place mainly at the 2- and 5-positions, which corresponds to the usual orientation in electrophilic substitution in heterocycles of this kind.

Ferrocene reacts with various olefins in the presence of palladium(II) acetate with formation of alkenylferrocenes [64-66]. The reactivity of olefins increases appreciably under the influence of electron-donating groups:



(X = Ph, CN, COOMe, CHO)

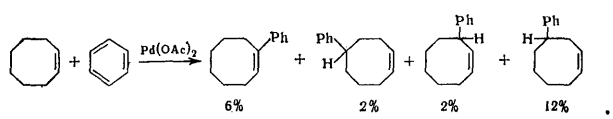
The arylation of olefins by triarylamines is an interesting example of the formation of compounds with functional groups as substituents [24]. The reaction with styrene gives rise to *trans*-*p*-diphenylaminostilbene:



Thus there is a significant difference between the behaviour of Ar_3N as an arylating agent and Ar_3E, where E = P, As, Sb, or Bi; in the presence of the latter stilbenes without a heteroatom are formed (see p. 553). Evidently this difference is due to the greater strength of the C–N bond than the bond between carbon and other Group VA elements.

The aryl group adds to asymmetric olefins preferentially at the least substituted carbon atom involved in the double bond, probably because of the steric hindrance of the substituents [67].

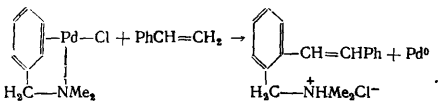
In contrast to acyclic olefins, cycloolefins give rise to a mixture of isomeric arylation products [68]:



The initial stage in the arylation of olefins is probably the formation of an organopalladium σ compound as a result of the direct combination of palladium with a benzene ring [43]:

$$PdX_2 + ArH \rightleftarrows [ArPdX] + HX$$

This is supported by Tsuji's data[69] concerning the formation of an arylated product in the reaction of the stable aryl σ complex between palladium and styrene:



The nature of the substituents in the aromatic system has a significant influence on the mode of substitution in the benzene ring. Electron-donating groups, for example alkyl groups, direct the substituents to the *o*- and *p*-positions, while electron-accepting groups (the nitro-group) are *m*-directing; chlorobenzene gives rise to a mixture of isomeric products with a high content of each isomer[70]. Hence the nature of the substituent hardly affects the reactivity of the aromatic compound.

On the other hand, the presence of polar groups in the olefin has a marked influence on the yields of the arylated products[71]. The reactivity of olefins decreases in the sequence

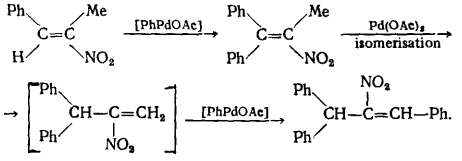
$$PhCH{=}CH_2 > NCCH{=}CH_2 > AcOCH{=}CH_2 > EtOCH{=}CH_2.$$

In arylation with heterocyclic aromatic compounds the inhibiting effect of electron-donating substituents in the olefin is also observed[31].

The reactivity of nitroolefins varies as follows[72]:

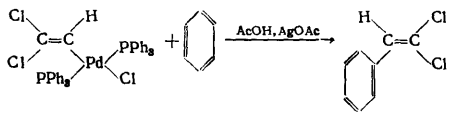
$$PhCH{=}CHNO_2 > CPhCH{=}CPhNO_2 > Ph_2C{=}CHNO_2.$$

It is noteworthy that the phenylation of β-methyl-β-nitrostyrene does not stop at the monoarylated product stage but leads to an olefin with two additional aryl groups[73];

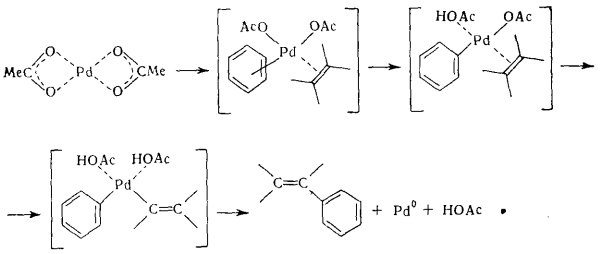


The absence of a substituent effect in the aromatic system on the rate of phenylation shows that the stage involving the formation of the aryl palladium σ complex is probably not rate-limiting. On the other hand, the marked influence of the substituents in the olefin suggests that the slow stage is the interaction of the olefin with palladium. However, the problem of the rate-limiting stage remains controversial. Thus the formation of an arylpalladium σ complex is believed[74] to be the rate-determining stage. This assertion is based on a study of the isotope effect in the arylation of olefins by deuteriobenzene in the presence of palladium(II) acetate.

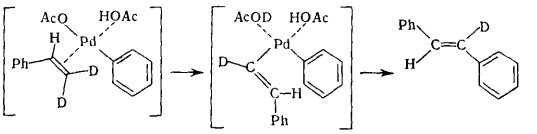
It has been suggested[71] that alkenylpalladium σ complexes take part in the arylation of unsaturated systems together with arylpalladium σ complexes. This is confirmed by the reaction of a stable vinylpalladium σ complex with benzene or toluene, which leads to the formation of an arylated olefin[75]:



Thus the mechanism of the reactions considered can be represented as follows[71]:



Indeed the study of the arylation of olefins in the presence of palladium using isotopes showed that, in contrast to the oxidation of olefins, there is no hydride shift in this reaction[76,77].



A similar study showed that the arylation of olefins by heterocyclic aromatic compounds also takes place without a hydride shift[33]. On the other hand, the mechanism of the substitution of unsaturated compounds with ferrocene includes a hydride shift stage[66].

The methods for the alkylation and arylation of olefins described above have been available for only a few years but they are nevertheless already of considerable preparative interest. Furthermore, the study of these reactions yields interesting information about the role of the formation of organometallic π and σ compounds in homogeneous catalysis.

REFERENCES

1. S. T. Ioffe and A. N. Nesmeyanov, "Metody Elementoorganicheskoi Khimii" (Methods in the Chemistry of Organic Derivatives of the Elements), Izd. Nauka, Moscow, 1963.
2. O. N. Temkin and R. M. Flid, "Kataliticheskie Prevrashcheniya Atsetilenovykh Soedinenii v Rastvorakh Kompleksov Metallov" (Catalytic Transformations of Acetylenic Compounds in Solutions of Metal Complexes), Izd. Nauka, Moscow, 1968.
3. I. I. Moiseev, "π-Kompleksy v Zhidkofaznom Okislenii Olefinov" (π-Complexes in the Liquid-phase Oxidation of Olefins), Izd. Nauka, Moscow, 1970.
4. I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, Dokl. Akad. Nauk SSSR, 133, 377 (1960).
5. I. I. Moiseev, M. N. Vargaftik, and Ya. K. Syrkin, Dokl. Akad. Nauk SSSR, 153, 140 (1963).
6. I. I. Moiseev and M. N. Vargaftik, Dokl. Akad. Nauk SSR, 166, 370 (1966).
7. R. F. Heck, J. Amer. Chem. Soc., 90, 5518 (1968).
8. R. F. Heck, J. Amer. Chem. Soc., 90, 5526 (1968).
9. R. F. Heck, J. Amer. Chem. Soc., 90, 5531 (1968).
10. R. F. Heck, J. Amer. Chem. Soc., 90, 5535 (1968).
11. R. F. Heck, J. Amer. Chem. Soc., 90, 5538 (1968).
12. R. F. Heck, J. Amer. Chem. Soc., 90, 5542 (1968).
13. J. B. Wilford, P. M. Treichel, and F. G. A. Stone, Proc. Chem. Soc., 1963, 218.
14. R. F. Heck, J. Amer. Chem. Soc., 85, 3116 (1963).

15. N. Garty and M. Michman, J. Organomet. Chem., **36**, 391 (1972).
16. M. Michman and M. Balog, J. Organomet. Chem., **31**, 395 (1971).
17. L. Farady, L. Bencze, and L. Marco, J. Organomet. Chem., **17**, 107 (1969).
18. R. J. P. Corriu and J. P. Masse, Chem. Comm., 1972, 144.
19. S. Uemura, J. Ikeda, and K. Ichikawa, Chem. Comm., 1971, 390.
20. H. Felkin and G. Swierczewski, Tetrahedron Letters, 1972, 1433.
21. I. S. Akrem, N. M. Chistovalova, and M. E. Vol'pin, Izv. Akad. Nauk SSSR, Ser. Khim., 1972, 1868.
22. I. S. Akhrem, N. M. Chistovalova, E. J. Mysov, and M. E. Vol'pin, J. Organomet. Chem., **72**, 163 (1974).
23. K. Kikukawa, T. Yamane, M. Takagi, and T. Matsuda, Chem. Comm., 1972, 695.
24. R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, Bull. Chem. Soc., Japan, **46**, 2910 (1973).
25. M. E. Vol'pin, I. Ya. Levitin, and L. G. Volkova, Izv. Akad. Nauk SSSR, Ser. Khim., 1971, 1124.
26. M. E. Vol'pin, L. G. Volkova, I. Ya. Levitin, N. N. Boronina, and A. M. Yurkevich, Chem. Comm., 1971, 849.
27. M. E. Vol'pin, R. Taube, H. Drevs, L. G. Volkova, I. Ya. Levitin, and T. M. Ushakowa, J. Organomet. Chem., **39**, c79 (1972).
28. R. F. Heck, J. Organomet. Chem., **37**, 389 (1972).
29. A. Kasahara, T. Izumi, G. Saito, M. Jodono, R. Saito, and Y. Goto, Bull. Chem. Soc. Japan, **45**, 895 (1972).
30. R. F. Heck, J. Organomet. Chem., **33**, 399 (1971).
31. L. S. Hegedus, E. L. Waterman, and J. Catlin, J. Amer. Chem. Soc., **94**, 7155 (1972).
32. J. Kim, T. Ukita, and T. Kwan, Tetrahedron Letters, 1972, 3079.
33. A. Kasahara, T. Izumi, M. Jodono, R. Saito, T. Takeda, and T. Sugawara, Bull. Chem. Soc. Japan, **46**, 1220 (1973).
34. A. Kasahara and T. Izumi, Bull. Chem. Soc. Japan, **45**, 1256 (1972).
35. R. F. Heck, J. Amer. Chem. Soc., **94**, 2712 (1972).
36. A. Kasahara, T. Izumi, and S. Ohnishi, Bull. Chem. Soc. Japan, **45**, 951 (1972).
37. T. Izumi, T. Iino, and A. Kasahara, Bull. Chem. Soc. Japan, **46**, 2251 (1973).
38. M. E. Vol'pin, A. M. Yurkevich, L. G. Volkova, E. G. Chauser, I. P. Rudakova, I. Ya. Levitin, E. M. Tachkova, and T. M. Ushakova, Zhur. Obshch. Khim., **45**, 164 (1975).
39. W. M. Scovell, J. Amer. Chem. Soc., **96**, 3451 (1974).
40. R. F. Heck, J. Amer. Chem. Soc., **91**, 6707 (1969).
41. R. F. Heck, J. Amer. Chem. Soc., **93**, 6896 (1971).
42. Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, Tetrahedron Letters, 1968, 633.
43. Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, Tetrahedron Letters, 1968, 3863.
44. T. Mizoroki, K. Mori, and A. Ozaki, Bull. Chem. Soc. Japan, **44**, 581 (1971).
45. K. Mori, T. Mizoroki, and A. Ozaki, Bull. Chem. Soc. Japan, **46**, 1505 (1973).
46. R. F. Heck and J. P. Nolly, J. Org. Chem., **37**, 2320 (1972).
47. M. E. Vol'pin, I. Ya. Levitin, L. G. Volkova, A. L. Sigan, and T. M. Ushakova, Izv. Akad. Nauk SSSR, Ser. Khim., 1973, 1205.
48. I. Moritani and Y. Fujiwara, Tetrahedron Letters, 1967, 1119.
49. Y. Fujiwara, I. Moritani, and M. Matsuda, Tetrahedron, **24**, 4819 (1967).
50. Y. Fujiwara, I. Moritani, M. Matsuda, and S. Teranishi, Tetrahedron Letters, 1968, 3863.
51. R. S. Shue, J. Catal., **26**, 112 (1972).
52. R. S. Shue, Chem. Comm., 1971, 1510.
53. R. van Helden and G. Verberg, Rec. Trav. Chim., **84**, 1263 (1963).
54. J. M. Davidson and C. Triggs, Chem. Ind. (London), 1966, 457.
55. J. M. Davidson and C. Triggs, Chem. Ind. (London), 1967, 1361.
56. J. M. Davidson and C. Triggs, J. Chem. Soc. (A), 1968, 1324.
57. J. M. Davidson and C. Triggs, J. Chem. Soc. (A), 1968, 1331.
58. S. Nishimura, T. Sakakibara, and Y. Odaira, Chem. Comm., 1969, 313.
59. J. Fujiwara, I. Moritani, K. Ikedami, R. Tanaka, and S. Teranishi, Bull. Chem. Soc. Japan, **43**, 863 (1970).
60. P. M. Henry, J. Org. Chem., **36**, 1886 (1971).
61. T. Sakakibara, S. Nishimura, K. Kimura, I. Minato, and I. Odaira, J. Org. Chem., **35**, 3884 (1970).
62. A. J. Bingham, L. K. Dyall, R. O. C. Norman, and C. B. Thomas, J. Chem. Soc. (C), 1970, 1879.
63. R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, Bull. Chem. Soc. Japan, **46**, 663 (1973).
64. R. Asano, I. Moritani, Y. Fujiwara, and S. Teranishi, Chem. Comm., 1970, 1293.
65. R. Asano, I. Moritani, A. Sonoda, Y. Fujiwara, and S. Teranishi, J. Chem. Soc. (C), 1971, 3691.
66. A. Kasahara and T. Izumi, Bull. Chem. Soc. Japan, **46**, 665 (1973).
67. Y. Fujiwara, I. Moritani, R. Asano, and S. Teranishi, Tetrahedron Letters, 1968, 6015.
68. I. Moritani, M. Yamamura, A. Sonoda, S. Teranishi, and Y. Fujiwara, J. Chem. Soc. (C), 1973, 203.
69. J. Tsuji, Acc. Chem. Res., **2**, 144 (1969).
70. Y. Fujiwara, I. Moritani, S. Danno, R. Asano, S. Teranishi, and H. Tanaka, Tetrahedron, **25**, 4815 (1969).
71. S. Danno, I. Moritani, and Y. Fujiwara, Tetrahedron, **25**, 4819 (1969).
72. K. Yamamura, S. Watarai, and T. Kinugasa, Chem. Lett., 1973, 91.
73. K. Yamamura, S. Waterai, and T. Kinugasa, Tetrahedron Letters, 1972, 2829.
74. R. S. Shue, J. Amer. Chem. Soc., **93**, 7116 (1971).
75. I. Moritani, Y. Fujiwara, and S. Danno, J. Organomet. Chem., **27**, 279 (1971).
76. S. Danno, I. Moritani, Y. Fujiwara, and S. Teranishi, J. Chem. Soc. (B), 1971, 196.
77. S. Danno, I. Moritani, and Y. Fujiwara, Chem. Comm., 1970, 610.

Institute of Organic Derivatives of the Elements, USSR Academy of Sciences, Moscow.