ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 1, pp. 1–17. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.V. Vasil'ev, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 1, pp. 9–24.

REVIEW

Alkenylation of Aromatic Compounds

A. V. Vasil'ev

St. Petersburg State Academy of Forestry Engineering, Institutskii per. 5, St. Petersburg, 194021 Russia
e-mail: aleksvasil@mail.ru

Received May 7, 2008

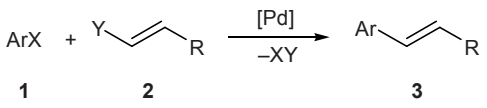
Abstract—The review summarizes new data on the introduction of alkenyl (vinyl) groups into aromatic and heteroaromatic structures via reactions with alkenes and alkynes. The main attention is given to the characterization and estimation of synthetic potential of the alkenylation of aromatic compounds with acetylene derivatives in the presence of transition metal complexes, as well as by the action of electrophiles, Lewis acids, and Brønsted superacids.

DOI: 10.1134/S1070428009010011

1. INTRODUCTION

Alkenylation of arenes, i.e., introduction of an alkenyl or vinyl group into aromatic and heteroaromatic systems, provides a synthetic route to derivatives of the styrene, stilbene, chalcone, cinnamic acid, and indene series, polycyclic heteroaromatic compounds, and other classes of organic compounds that are important from the viewpoints of both fundamental studies and practical application. Classical alkenylation methods include reactions of aromatic compounds **1** with alkenes or their functional derivatives **2**, catalyzed by palladium complexes, which lead to the formation of arylalkenes **3** (Scheme 1).

Scheme 1.



1 **2** **3**

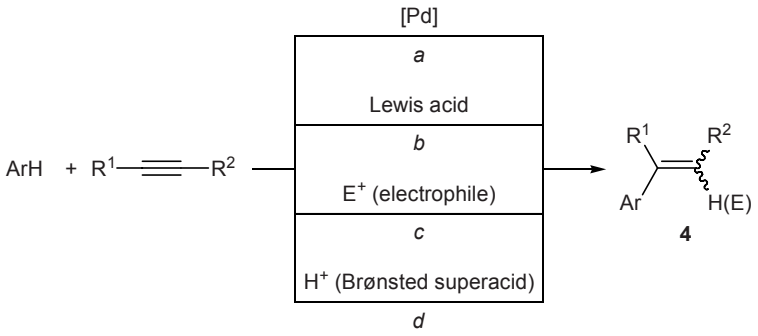
(*a*) Heck–Mizoroki reaction: X = Cl, Br, I, OTf; Y = H; (*b*) Suzuki–Miyaura reaction: X = BR'_2, BF_3^-; Y = Cl, Br, I, OTf; or X = Cl, Br, I, OTf; Y = BR'_2, BF_3^-; (*c*) Stille reaction: X = Cl, Br, I; Y = SnR_3; (*d*) Negishi reaction: X = ZnCl, ZnBr; Y = Cl, Br, I, OTf.

However, in the recent years other approaches have been extensively developed on the basis of reactions of aromatic compounds with alkynes. According to these approaches, alkenylation products **4** can be obtained in several ways, including (*a*) catalysis by transition metal complexes and activation of triple carbon–carbon bond by (*b*) Lewis acids, (*c*) electrophilic reagents, and (*d*) Brønsted superacids (Scheme 2). These reac-

Aleksandr Viktorovich Vasil'ev was born in 1970 in Leningrad. In 1992, he graduated from the Faculty of Chemistry, St. Petersburg State University. Candidate of chemical sciences, assistant professor at the Organic Chemistry Department, St. Petersburg State Academy of Forestry Engineering.

Fields of scientific interest: chemistry of acetylenic compounds, chemistry of organic compounds in superacids, radical cations and charge-transfer complexes derived from organic compounds, new methods of building up carbon–carbon bonds, and synthesis of analogs of natural compounds.

Scheme 2.



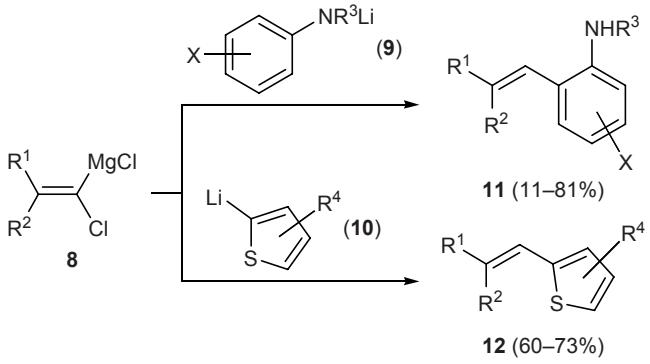
tions can also be regarded as hydroarylation of acetylenic bond.

The present review analyzes the synthetic potential of new methods for alkenylation of aromatic compounds with alkenes and alkynes with a specific emphasis given to reactions involving acetylenic compounds.

2. ALKENYLATION OF AROMATIC COMPOUNDS WITH ALKENES

Up to now, the conditions, specific features, and mechanisms of the formation of arylalkenes **3** according to Scheme 1 have been explored in sufficient detail, and relevant data are summarized in reviews on the Heck–Mizoroki [1–9], Suzuki–Miyaura [6, 7, 9–11], Stille [9, 12, 13], and Negishi reactions [14–16]. In addition to these palladium-catalyzed processes, alkenylation of arenes can be performed in other ways using various functsionally substituted alkenes. Among recent developments in this field, iron(III)-catalyzed reactions of arylmagnesium halides **5** with a large number of vinyl triflulromethanesulfonates **6** to give compounds **7** [17] must be noted (Scheme 3). Oxidation of Grignard compounds **5** with Fe^{3+} ions generates highly reactive nucleophilic species $[Fe(MgX)_2]_n$ which catalyze further reaction of **5** with **6**. Vinyl-type Grignard compounds **8** were reported to react with lithium anilides **9** and α-lithiated thiophenes **10**, yielding compounds **11** and **12**, respectively [18–20] (Scheme 4). Aniline derivatives **9** react in selective fashion to give only *ortho*-alkenyl-substituted products **11** [18, 19].

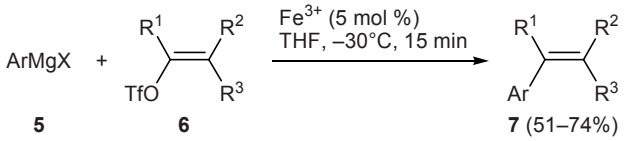
Scheme 4.



R^1, R^2 = Alk, alkenyl, Ph; R^3 = H, Me; R^4 = H, 5-Me, 5-MeO, 5-Cl, 2,3-benzo; X = H, 2(3,4)-Me, 2,6-Me_2, 3(4)-MeO, 3(4)-Cl, 3-CN, 2,3-benzo.

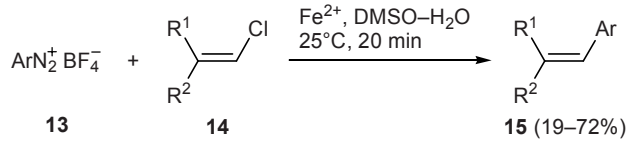
Decomposition of diazonium salts **13** by the action of Fe^{2+} ions generates intermediate aryl radicals which react with vinyl chlorides **14** to produce derivatives of styrene, stilbene, and cinnamic acid (**15**, Scheme 5) [21]. An interesting procedure for the introduction of vinyl groups into aromatic systems was proposed by Amatore et al. [22]. Aryl chlorides or bromides **16** reacted with vinyl acetates **17** in the presence of metallic manganese and 5 mol % of $CoBr_2$. The catalytic series includes reduction of Co(II) to Co(I) or Co(0) with manganese. Low-valence or zero-valence cobalt reacts

Scheme 3.



X = Cl, Br; Ar = Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4; R^1, R^2, R^3 = Alk, Ar; R^2 = CO_2Et.

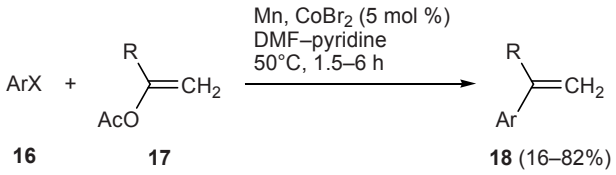
Scheme 5.



R^1 = H, Cl, CO_2Et; R^2 = H, Cl, 4-$MeOC_6H_4$; Ar = $R^3C_6H_4$; R^3 = 4-MeO, 4-F, 2-CO_2Me.

with aryl halides **16** to give arylcobalt compounds as key intermediates in the synthesis of target products **18** (Scheme 6).

Scheme 6.



16 **17** **18** (16–82%)

X = Cl, Br; R^1 = H, Alk; Ar = $C_6H_4R^2$, R^2 = 2(3,4)-CO_2Me(Et), 2(4)-COMe, 2(3,4)-CN, 2(3,4)-MeO, 4-AcO, 4-Me_2N.

An intramolecular version of the Ullmann reaction [9], i.e., cross coupling of two sp^2-carbon atoms (aryl and vinyl) attached to halogen, was utilized in the synthesis of cyclic ethers using a catalytic system composed of Pd/C and metallic indium [23]. The above new procedures for the alkenylation of aromatic compounds with alkenes are characterized by high regio- and stereoselectivity [17–23].

3. ALKENYLATION OF AROMATIC COMPOUNDS WITH ALKYNES

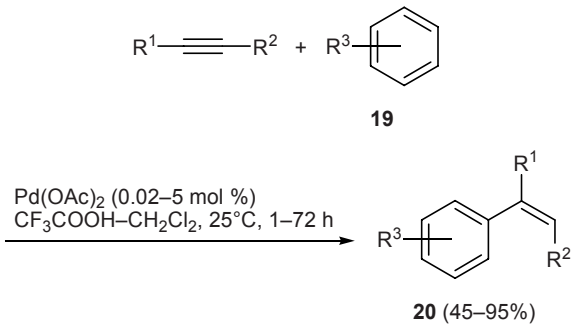
This section considers alkenylation of arenes with acetylenic compounds using various reagents and catalysts. The importance and prospects in the application of these procedure follow from their extensive use in organic synthesis [24–31].

3.1. Reactions Catalyzed by Transition Metal Complexes

3.1.1. Alkyne insertion into aromatic C–H bonds. In 2000, Fujiwara and co-workers [32–35] reported on alkyne insertion into C_{arom}–H bonds in arenes **19** to give alkenylation products **20** under catalysis by palladium(II) or platinum(II) compounds in the presence of trifluoroacetic acid (Scheme 7). The reaction readily occurs with benzene and its derivatives activated by donor substituents, such as *p*-xylene, mesitylene, durene, pentamethylbenzene, phenols, alkyl phenyl ethers, and naphthalene. Depending on the substitution pattern, arenes **19** react according to the orientation rules typical of aromatic electrophilic substitution.

Phenylacetylene as acetylene component gives rise to alkenylation products **20** (R^1 = Ph, R^2 = H) formally conforming to the Markovnikov rule; oct-4-yne, diphenylacetylene, and methylphenylacetylene were also used; the latter reacted in such a way that hydrogen

Scheme 7.



20 (45–95%)

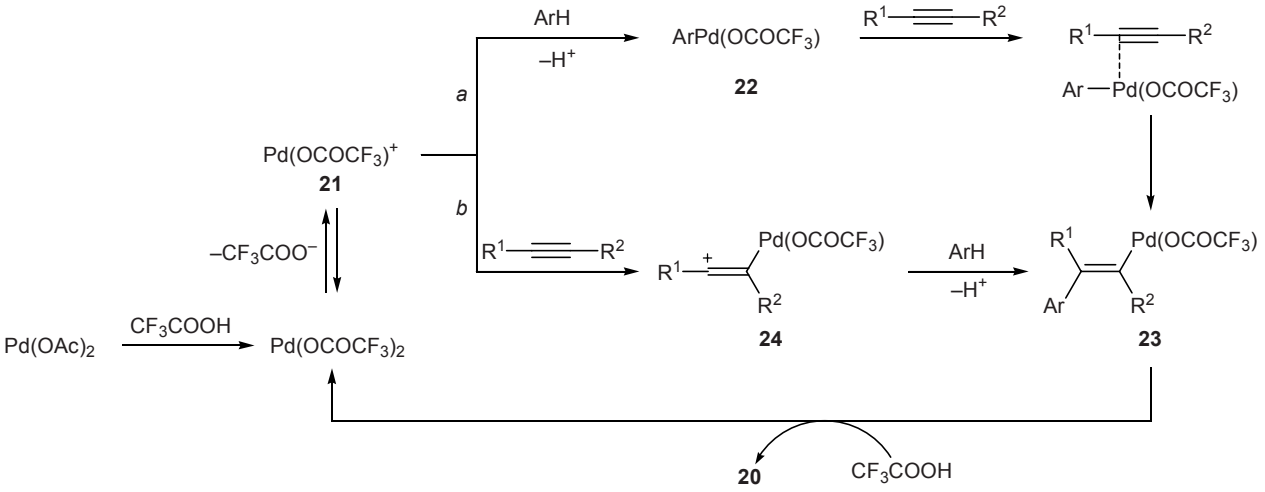
R^1 = H, Me, Pr, Ph, CO_2Et; R^2 = H, Pr, Ph, CO_2H, CO_2Et, CHO, COMe; R^3 = H, Me_n (n = 1–5), 4-*t*-Bu, $(MeO)_n$ (n = 1–3), 4-OH, 3,4-OCH_2O, 2,3-benzo.

atom added to C^2 to form compound **20** with R^1 = Ph and R^2 = Me. Furthermore, conjugated acetylenic aldehydes, ketones, and carboxylic acids and their esters containing a $C^3{\equiv}C^2{-}C^1{=}O$ fragment were involved; in these cases, the aryl group selectively added to C^3, as in the Michael reaction [32]. The alkenylation gives mainly *anti*-addition products **20**. An exception was but-3-yn-2-one which gave rise to only *syn*-adducts. The yields of compounds **20** mostly exceed 45%, in many cases reaching 90–95% [32].

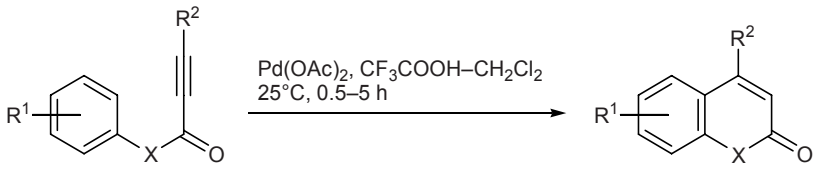
The mechanism of this reaction [31] includes generation *in situ* of electrophilic species **21** from palladium(II) acetate and trifluoroacetic acid. This species, i.e., palladium(II) monotrifluoroacetate, can react further along two pathways. Its reaction with an arene (pathway *a*) gives σ-arylpalladium complex **22** which takes up an alkyne to produce intermediate **23**. The latter can also be formed via addition of cation **21** at the triple bond of alkyne through intermediate formation of vinyl-type cation **24** and subsequent electrophilic aromatic substitution of hydrogen in ArH. In the last step, the $[PdO_2CCF_3]^+$ group in **23** is replaced by proton, yielding final product **20** (Scheme 8). It is not always possible to determine which path (*a* or *b*) is operative in each particular case [31]. However, measurement of kinetic H/D isotope effects showed that path *b* predominates in some intramolecular alkenylation processes [35].

Intramolecular version of this reaction ensures preparation of substituted coumarins **26** (X = O) and quinolin-2(1*H*)-ones (X = NH) from phenyl acetylenecarboxylates and *N*-arylacetylenecarboxamides **25**, respectively [33, 36] (Scheme 9). Coumarin derivatives **29** can also be synthesized by reaction of phenols **27** with acetylenecarboxylic acids or their esters **28** [33, 37–39] (Scheme 10). Initially, new C–C bond is

Scheme 8.



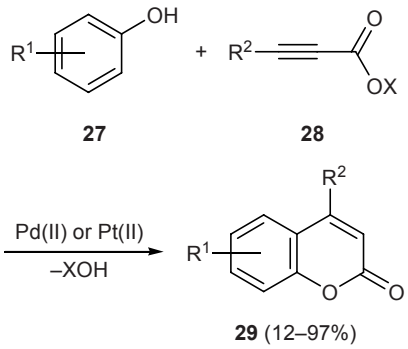
Scheme 9.



X = O, NH; R^1 = Me_n (n = 1, 2), 4-*t*-Bu, $(MeO)_n$ (n = 1–3), 3,4-OCH_2O, 2,3-benzo; R^2 = H, Me, C_5H_{11}, Ph.

formed between the *ortho*-carbon atom in phenol **27** and triple-bonded C^3 atom in **28**, and subsequent intramolecular esterification (or transesterification) yield coumarins **29**. Such reactions were reported for phenol [39], methoxy- and methylenedioxy-substituted phenols [33, 37–39], and 2-naphthol [37, 39].

Scheme 10.

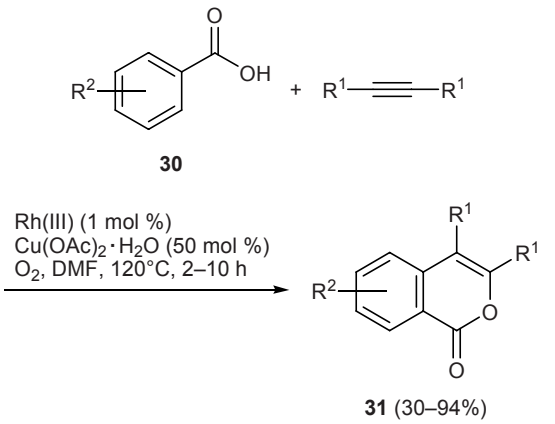


X = H, Me, Et; R^1 = H, Me_n (n = 1, 2), 4-*t*-Bu, $(MeO)_n$ (n = 1–3), 3,4-OCH_2O, 2,3-benzo; R^2 = H, Me, C_5H_{11}, Ph, CO_2Et.

Ueura et al. [40, 41] reported on the synthesis of a series of isocoumarin derivatives **31** by coupling of benzoic acids **30** with internal alkynes in the presence of rhodium(III) complexes and copper(II) salts on exposure to atmospheric air (Scheme 11). Benzoic acids **30** having both electron-donating and electron-withdrawing substituents R^2 can be involved.

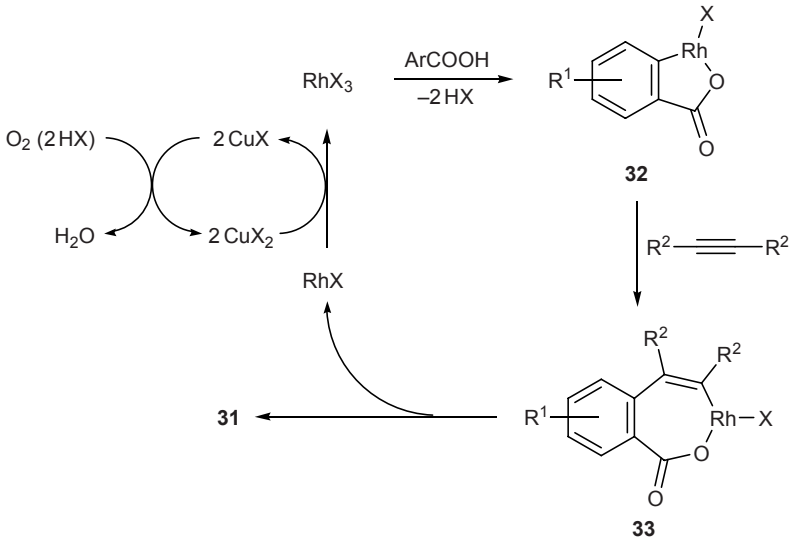
The mechanism of formation of isocoumarins **31**, proposed in [40, 41], includes initial generation of cyclic rhodium intermediate **32** (cf. path *a* in Scheme 8), followed by alkyne insertion into the C_{arom}–Rh bond to

Scheme 11.



R^1 = Alk, Ph; R^2 = H, 2(3,4)-Me, 2-Ph, 4-Cl, 4-OH, 4-CF_3, 3,5-$(MeO)_2$.

Scheme 12.



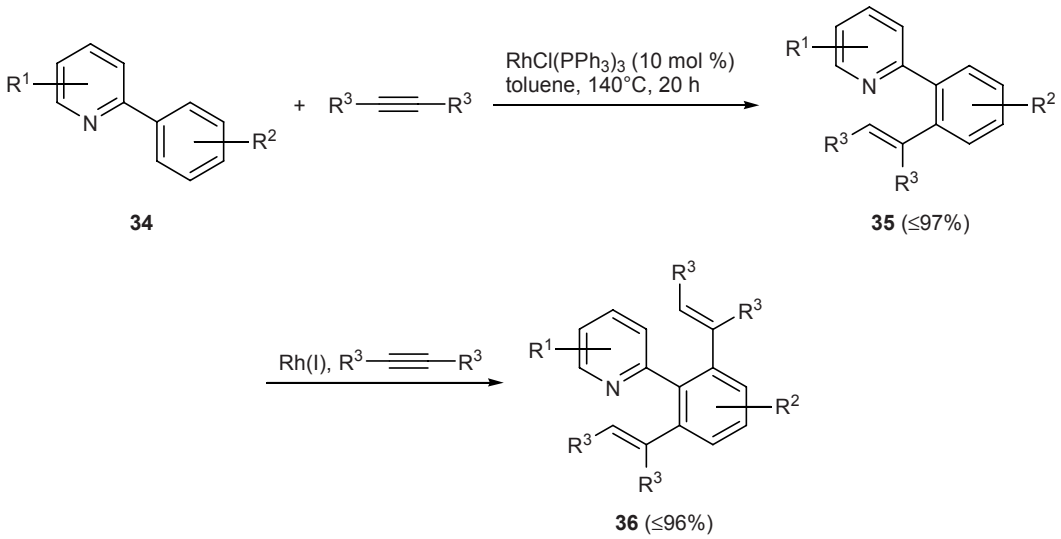
give structure **33** and reductive elimination of RhX from the latter, yielding final product **31**. The role of Cu(II) in the catalytic series is to oxidize Rh(I) to reactive Rh(III); Cu(I) is then oxidized to Cu(II) by the action of atmospheric oxygen (Scheme 12).

Hong et al. [42] were the first to report on the use of rhodium complexes in the alkenylation of arenes. Rhodium carbonyl complexes promoted the reaction of benzene with diphenylacetylene in carbon(II) oxide atmosphere to produce a mixture of 1,1,2-triphenylethene (45%) and 2,3-diphenylindan-1-one (10%). However, these studies have not received due attention because of extreme conditions (gaseous CO under pressure, high temperature), and only recently rhodium catalyst have been used again in the alkenylation of aromatic compounds [40, 41, 43, 44].

Rhodium-catalyzed reactions of 2-arylpyridines **34** with symmetric internal alkynes lead to the formation of mono- or dialkenyl-substituted products **35** and **36**, depending on the reactant ratio; in both cases, alkenyl group enters the *ortho* position with respect to the pyridyl substituent [43]. Most reactions follow the *syn*-addition pattern (Scheme 13).

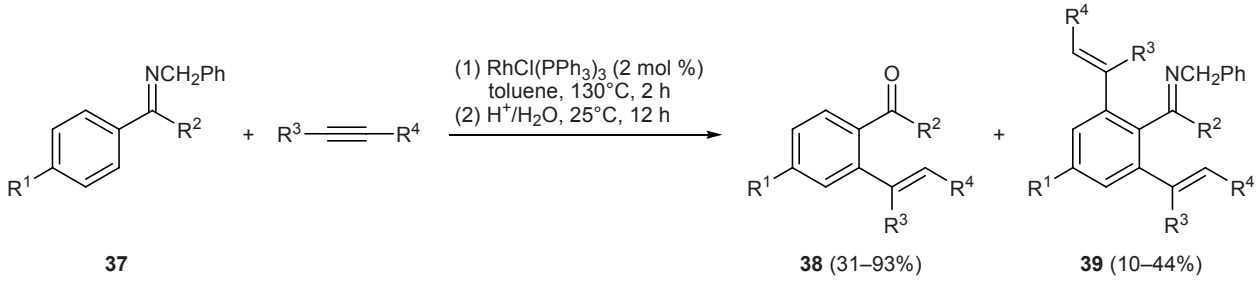
Analogous *ortho*-alkenylation of *N*-benzyl acetophenone imines **37** with alkynes yields the corresponding *syn*-addition products **38** and **39** [44] (Scheme 14).

Scheme 13.



R^1 = H, 3-Me; R^2 = H, 2-Me, 4-Me, 2-*t*-BuCH_2CH_2; R^3 =Alk, Ph.

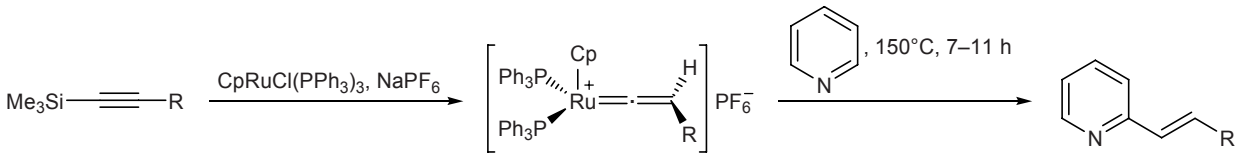
Scheme 14.



37 **38** (31–93%) **39** (10–44%)

R^1 = H, MeO, CF_3; R^2 = H, Et, C_5H_{11}; R^3 = H, Ph; R^4 = Bu, *t*-Bu, C_6H_{13}, Ph.

Scheme 15.



40 **41** **42** (75–92%)

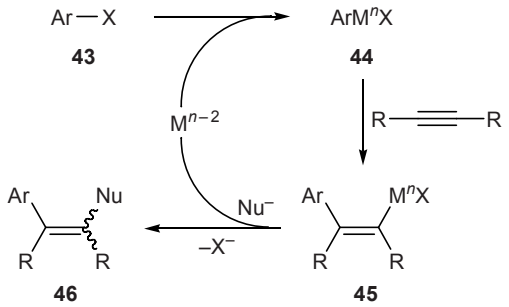
R = C_5H_{11}, Ph, 4-MeC_6H_4, cyclohex-1-en-1-yl.

Terminal acetylenes (R^3 = H) give rise to formal anti-Markovnikov adducts **38** and **39**, presumably due to different stabilities (ease of formation) of rhodium intermediates like **33** [44]. Acid treatment of the reaction mixtures induces facile hydrolysis of monoalkenylation products to ketones **38**. Such rhodium-catalyzed reactions are generally characterized by introduction of alkenyl substituent exclusively into the *ortho* position with respect to the oxygen- or nitrogen-containing group (Schemes 12–14). The presence of oxygen or nitrogen atom favors formation of reactive cyclic rhodium intermediates analogous to structure **32**.

Ruthenium-catalyzed reactions [45] are mediated by vinylidene complexes **41** generated from trimethylsilylacetylenes **40** [46] (Scheme 15). Complexes **41** react with pyridine with high regio- and stereoselectivity to give *trans*-isomeric 2-alkenylpyridines **42**. The catalytic system Ni(II)–P(*i*-Pr)$_3$–$ZnMe_2$ was also successfully used to effect alkenylation of substituted pyridines at the α-position with internal alkynes [47].

3.1.2. Insertion of alkynes into C–X bonds (X = Hlg, CN, BR_2, etc.) of arenes. A particular group of alkenylation reactions includes transition metal-catalyzed insertion of alkynes into C_{arom}–X bonds (X = Hlg, CN, BR_2, etc.) of aromatic compounds. The mechanism of these reactions implies initial formation of σ-arylmetal complex **44** from arene **43** [27], followed by insertion of alkyne into the C_{arom}–M^n bond of complex **44**, leading to structure **45**. The latter reacts with nucleophile Nu^-, and the subsequent reductive elimination regenerates catalytically active form M^{n-2} and yields product **46** (Scheme 16). Here, nucleophiles Nu^- may be hydride ion donors or oxygen-, nitrogen-, and carbon-centered nucleophiles.

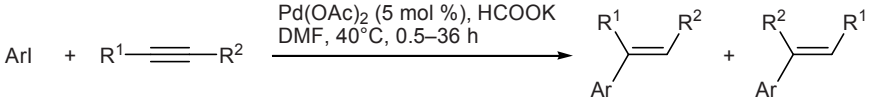
Scheme 16.



X = Cl, Br, I, CN, BR_2, N_2^+, $SnBu_3$, CR_2OH, COSAr; Nu = H, O, C, N, etc.; M^n = Pd(II), Ni(II), Pt(II), Rh(III), Co(II).

Alkenylation of aryl iodides with alkynes catalyzed by $Pd(OAc)_2$ without phosphine ligands gives mixtures of isomeric alkenes **47** and **48** [48, 49] (Scheme 17), products of *syn* addition at the acetylenic bond prevailing. The regioselectivity of this reaction is controlled mainly by steric factors: aryl group adds at the less sterically loaded triple-bonded carbon atom in the initial acetylenic compound. 4-Phenylbut-3-yn-2-one gives rise exclusively to *E*/*Z*-isomeric anti-Michael adducts **47** (R^1 = COMe, R^2 = Ph) [48]. Potassium formate acts as reducing agent (hydride ion donor). The reaction can be performed with various aryl

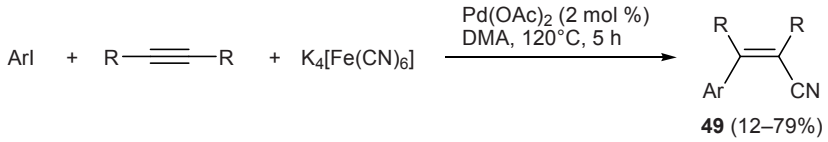
Scheme 17.



47 (12–79%) **48**

R^1, R^2 = Alk, Ph, COMe, $CH(OEt)_2$; Ar = Ph, 4-MeC_6H_4, 3-FC_6H_4, 4-HOC_6H_4, 4-$MeOC_6H_4$, 4-$H_2NC_6H_4$, 4-$AcNHC_6H_4$, 4-$MeCOC_6H_4$, 4-$MeOCOC_6H_4$, 3-$O_2NC_6H_4$.

Scheme 18.



49 (12–79%)

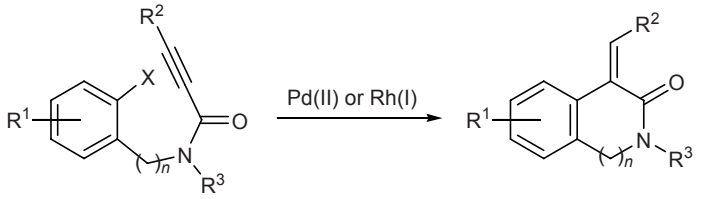
R = *n*-Pr, *n*-Bu, Ph, 4-MeC_6H_4; Ar = Ph, 2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 4-$Me_2NC_6H_4$, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$, 3-ClC_6H_4, 1-$C_{10}H_7$.

iodides containing both electron-donating and electron-withdrawing groups.

A procedure for the synthesis of 4-arylchromenes via reaction of aryl iodides with acetylenic alcohols was reported in [50]. The products attract interest as medical agents. Unsaturated nitriles **49** were synthesized from aryl iodides and symmetric internal alkynes in the presence of $K_4[Fe(CN)_6]$ as source of nucleophilic cyanide ions [51] (Scheme 18). The corresponding *syn* adducts are formed with high stereoselectivity.

Intramolecular alkenylation of acetylenecarboxamides **50** opens a way to various nitrogen-containing heterocycles **51** [52–54], including pharmacologically important benzoazepine derivatives **51** (n = 2) [53] (Scheme 19). Larock and co-workers developed a specific synthetic approach to heterocyclic compounds [27] on the basis of palladium-catalyzed alkenylation

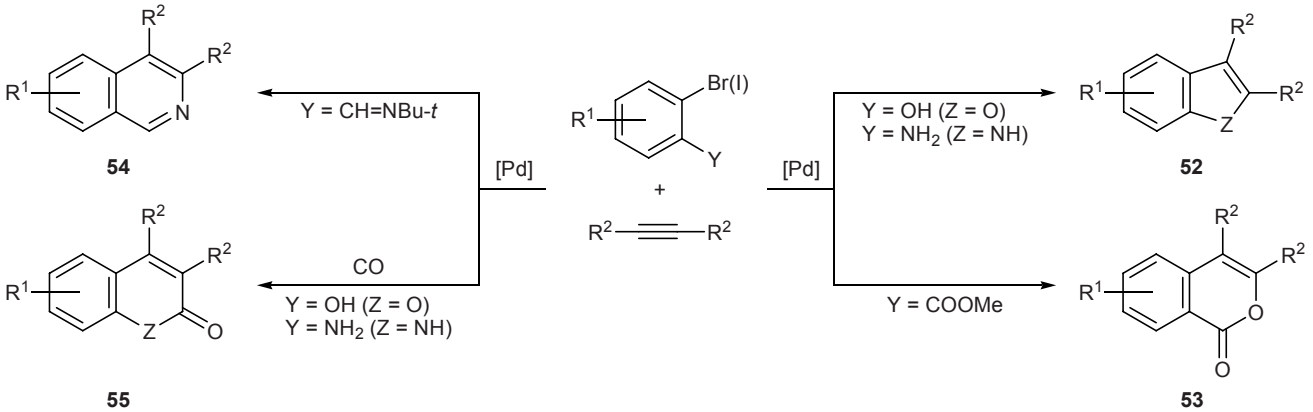
Scheme 19.



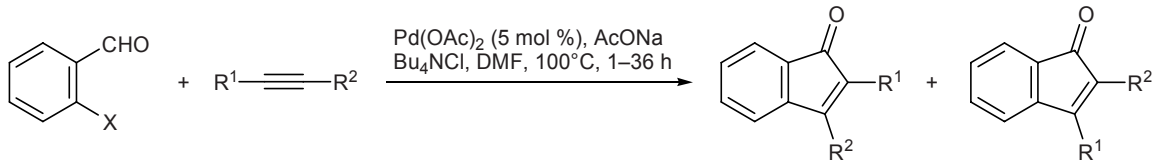
50 **51** (≤95%)

n = 0–3; X = Cl, Br, I; R^1 = H, $(MeO)_m$ (m = 1, 2); R^2, R^3 = H, Alk, Ar.

Scheme 20.



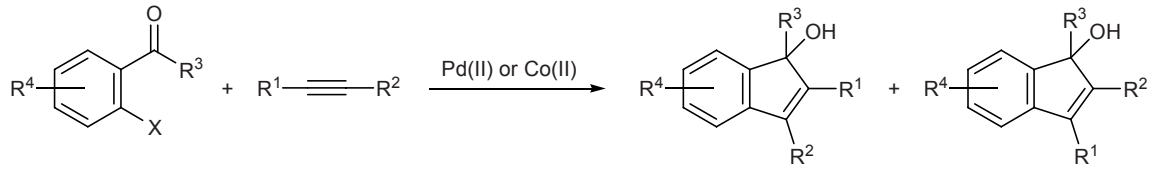
Scheme 21.



56 (45–99%)

X = Br, I; R^1, R^2 = Alk, Me_3Si, Ar.

Scheme 22.



57 (45–99%) **58**

X = Br, I; R^1, R^2 = Alk, Ar, $MeOCH_2$, Me_3Si, CO_2Me; R^3 = H, Me, Pr, Bu, Ph, 4-$CF_3C_6H_4$, 4-$MeOC_6H_4$; R^4 = H, 4-*t*-Bu, $(MeO)_n$ (*n* = 1–3), 4,5-OCH_2O.

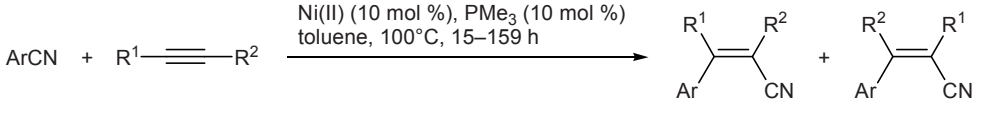
of *ortho*-halogen-substituted phenols, anilines, benzoic acid esters, and *N*-*tert*-butyl benzaldehyde imines with internal alkynes. Following this approach, the authors synthesized derivatives of the benzofuran (**52**, Z =O), isocoumarin (**53**) [55], indole (**52**, Z = NH) [56], quinoline (**55**, Z = NH; in combination with carbonylation) [57], isoquinoline (**54**) [58], and coumarin series (**55**, Z = O; in combination with carbonylation) [59] (Scheme 20), as well as various polyheterocyclic compounds [60]. The reactions were characterized by high yields [27]. Likewise, carbocyclic systems **56** of the indene series were obtained from *ortho*-halobenzaldehydes and alkynes [61] (Scheme 21). Analogous reactions of *ortho*-haloacetophenones afforded isomeric hydroxyindenes **57** and **58** [62–64] (Scheme 22). Unlike palladium-catalyzed reactions [61], benzaldehydes were converted into hydroxyindenes **57** and **58** under catalysis by Co(II) complexes [63].

If initial acetylenic compound has different substituents at the triple bond ($R^1 \neq R^2$), mixtures of two isomeric indenones **56** [61] or hydroxyindenes **57**/**58** [63] are usually obtained. The isomer ratio depends on both steric factor [61] and electronic properties of the R^1 and R^2 substituents [63, 64] in intermediate palladium or cobalt complexes. Bulky substituents, such as *t*-Bu, CMe_2OH, and $SiMe_3$ groups, appear in position *2* of the indene system in products **56** [61]. Among isomers **57** and **58**, those having strong electron-withdrawing groups on C^2 (R^1 or R^2 = CO_2Me, CO_2Et) predominate [63].

An interesting procedure for the synthesis of 2,3-di- (or 2-mono)substituted indenes was developed on the basis of reaction of *ortho*-bromobenzylzinc bromide with various acetylenic substrates in the presence of Ni(II) complexes as catalysts [65].

Alkenylation can also be performed with functionalized arenes ArX (**43**), e.g., aromatic nitriles (X = CN). For example, aromatic and heteroaromatic nitriles react with acetylenes in the presence of Ni(II) complexes to give the corresponding alkenes **59** with *trans*-oriented aryl (hetaryl) and cyano groups [66–68] (Scheme 23). Aromatic nitriles having both electron-donating and electron-withdrawing substituents are active in this process. The cyano group in the initial

Scheme 23.



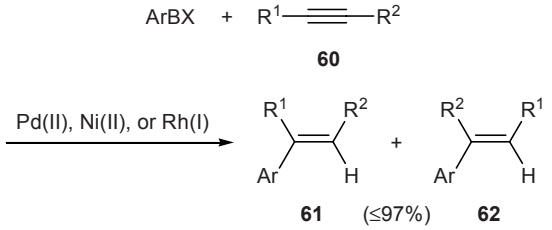
59 (36–96%)

R^1, R^2 = Alk, Me_3Si; Ar = Ph, 4-MeC_6H_4, 4-BrC_6H_4, 4-ClC_6H_4, 4-PhC_6H_4, $(MeO)_nC_6H_{5-n}$ (*n* = 1–3), 2-$CF_3C_6H_4$, 4-$MeCOC_6H_4$, 4-$MeOCOC_6H_4$, 4-$OCHC_6H_4$, 2-furyl, 2-thienyl, pyridin-2(3,4)-yl.

nitrile acts as nucleophilic species Nu^-. Unsymmetrical acetylenes ($R^1 \neq R^2$) give rise to mixtures of two regioisomeric nitriles **59**; here, the major isomer is that in which bulkier substituent R^1 or R^2 is attached to the carbon atom bearing the cyano group [66, 68].

A general method for the synthesis of styrene, stilbene, and cinnamic acid derivatives **61** and **62** is based on the reaction of aromatic organoboron compounds with alkynes, catalyzed by Pd(II), Ni(II), and Rh(I) complexes [69–74]. The reaction involves stereoselective *syn*-addition at the triple C≡C bond. Sterically unhindered terminal acetylenes **60** (R^2 = H) react to produce formal Markovnikov adducts **61** [69, 71]. Unsymmetrical internal acetylenes **60** ($R^1 \neq R^2$) give rise to mixtures of isomers **61** and **62** whose ratio depends on the steric and electronic properties of the R^1 and R^2 substituents [70, 71] (Scheme 24). The aryl group in the organoboron compound adds mainly at the less sterically hindered triple-bonded carbon atom in **60** [70, 71]. The corresponding Michael adducts **61** (R^2 = CO_2Me, CO_2Et) are formed as the major products from alkyl acetylenedicarboxylates **60** (R^2 = CO_2Me, CO_2Et) [71].

Scheme 24.



X = $(HO)_2$, $(RO)_2$, Ph_3Na; R^1, R^2 = H, Alk, Ph, CO_2Alk.

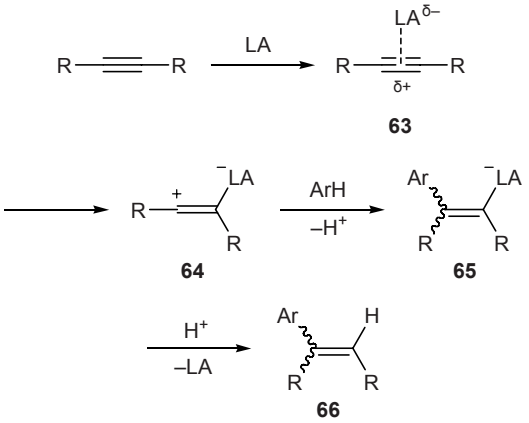
Apart from aryl halides, aromatic nitriles, and organoboron derivatives, other functionalized ArX compounds can be subjected to alkenylation, in particular those with X = N_2^+ [74], $SnBu_3$ [75], CR_2OH [76], and COSAr [77]. Alkyne insertion into the corresponding C_{arom}–X bonds is catalyzed by palladium [74–76] and platinum complexes [77].

Thus reactions of arenes with acetylenic compounds, catalyzed by transition metal complexes (Pd, Pt, Rh, Ru, Ni, Co) underlie a number of highly efficient methods for the introduction of alkenyl substituents into aromatic and heteroaromatic systems. Inter- and intramolecular reactions of this type involve broad ranges of structurally diverse aromatic and acetylenic substrates. In many cases intermolecular alkenylation processes are characterized by good stereoselectivity, and they give mainly the corresponding products of *syn*-addition at the triple C≡C bond.

3.2. Reactions Catalyzed by Lewis Acids

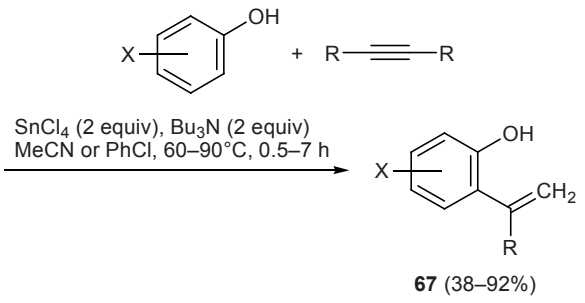
Coordination of a Lewis acid at a triple C≡C bond provides electrophilic activation of acetylenic carbon atoms in species like **63**. In the limiting case, formation of vinyl-type cation **64** is possible, and its subsequent reaction with an aromatic compound could give structure **65** and then final product **66** [28, 30] (Scheme 25). Various compounds can act as Lewis acids in such reactions, in particular Al(III), Sn(IV), Ga(III), Fe(III), In(III), Sc(III), Pt(II), Pt(IV), Au(I), Au(III), and other compounds.

Scheme 25.



Yamaguchi et al. [78, 79] were among the first who reported on effective application of Lewis acid in the alkenylation of arenes. Acetylene and terminal alkynes regioselectively reacted with phenols in the presence of tin(IV) chloride in combination with tributylamine to give *o*-vinylphenols **67** (Scheme 26). However, this

Scheme 26.

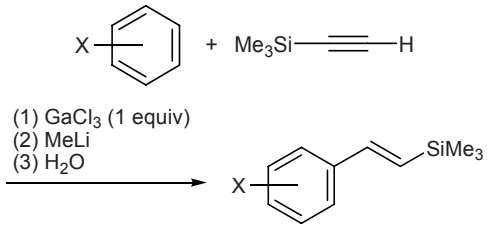


X = H, 2(3,4)-Me, 2(3,4)-*t*-Bu, 2(3,4)-MeO, 2(3,4)-F, 4-Cl, 4-Me_2N, 2(4)-F, 2(4)-CN, 3(4)-O_2N; R = H, C_5H_{11}, Ph, $Ph(CH_2)_2$, 4-$MeOC_6H_4$.

reaction cannot be performed with internal alkynes, for probable intermediates were postulated to be alkynyl(trichloro)tin derivatives which can be generated only from terminal acetylenes.

Gallium(III) chloride was used to catalyze alkenylation of polymethyl- and polymethoxy-substituted benzenes, naphthalene, and other polycyclic aromatic hydrocarbons with trimethylsilylacetylene [80–82]. The products were the corresponding anti-Markovnikov adducts **68** (Scheme 27) owing to electronic effect of the trimethylsilyl group on the positive charge distribution over acetylenic carbon atoms in cationic intermediates analogous to structure **63** [80] (a similar pattern of the addition to trimethylsilylalkynes was described in [78]). The trimethylsilyl group in compounds **68** can readily be replaced by hydrogen upon treatment with trifluoroacetic acid, which opens a way to a series of substituted styrenes.

Scheme 27.

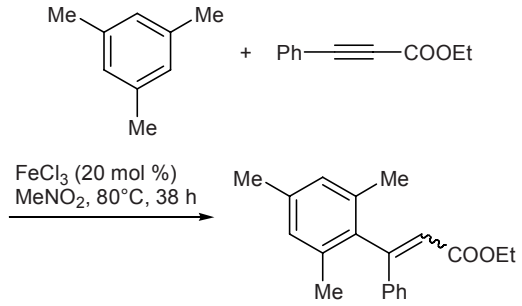


68 (41–76%)

X = Me_n (n = 1–3), $(MeO)_n$ (n = 1–3), 2,3-benzo.

Iron(III) chloride as Lewis acid makes it possible to perform alkenylation with a broader series of acetylenic compounds, including phenylpropynoic acid derivatives in which the basicity of the triple C≡C bond is reduced. These reactions give mainly *anti*-addition products [83] (Scheme 28). Platinum chlorides $PtCl_2$ [84] and $PtCl_4$ [85] are also Lewis acids capable of coordinating at triple bond in alkynes. The system

Scheme 28.



Z (*anti*) : *E* (*syn*) = 94 : 6 (42%)

$PtCl_2$–AgOTf catalyzed alkenylation of polymethyl- and hydroxy-substituted benzenes, as well as of naphthalene, with ethyl propynoate to produce *cis*-3-arylprop-2-enoates in regio- and stereoselective fashion [84]. Platinum(IV) chloride was used as catalyst in the intramolecular cyclization of acetylenic ethers to obtain heterocyclic compounds of the chromene series [85–87]. Platinum chloride-catalyzed intra- [88] and intermolecular [89] alkenylation of aromatic systems with acetylenic compounds underlay methods for the synthesis of biologically active coumarin and pyrrole derivatives.

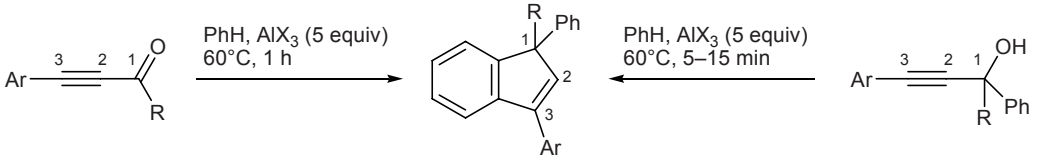
In the recent time, gold(I) and gold(III) complexes have been extensively used in organic synthesis as catalysts ensuring electrophilic activation of various organic substrates [90–92]. Gold chlorides $AuCl_3$ and AuCl have found application as Lewis acids promoting reactions of alkynes with arenes [93–97]. In these reactions, alkenylation occurred only with electron-rich aromatic π-systems such as polyalkyl-, hydroxy-, and methoxy-substituted benzene and naphthalene derivatives [93–95], as well as furans [96] and indoles [97]. Gold chlorides were shown to activate alkyl- and arylacetylenes [93, 95, 96], conjugated acetylenic ketones, and alkyl propynoates [93, 94]. Among the alkenylation products, those resulting from *anti*-addition at the C≡C bond prevailed [93, 94].

Such Lewis acids as Sc(III), In(III), Zr(IV), Hf(IV), Lu(III), Y(III), and Yb(III) trifluoromethanesulfonates catalyzed alkenylation of benzene and its polymethyl-, halogen-, and methoxy-substituted derivatives with aryl- and diarylacetylenes [98–101]. Metal trifluoromethanesulfonates favored predominant *anti*-addition of hydrogen and aryl group at the triple bond [98–100].

The catalytic activity of $Sc(OTf)_3$, $In(OTf)_3$, and $Hf(OTf)_3$ considerably increases in the presence of ionic liquids [99]. Moreover, Choi et al. [100] reported that even a catalytic amount (5 mol %) of a ionic liquid based on 1-butyl-3-methylimidazolium catalyzed alkenylation of arenes with acetylenic compounds in the absence of metal trifluoromethanesulfonate. The use of ionic liquids made it possible to perform alkenylation with acetylenic compounds in which the triple bond is conjugated with an electron-withdrawing group, in particular with acetylenecarboxylic acid amides and esters [99] and but-3-yn-2-one [100].

Such Lewis acids as $AlBr_3$ and $AlCl_3$ have recently been reported to catalyze reactions of acetylenic carbonyl compounds **69** or α,β-acetylenic alcohols **70** with benzene to give substituted indenes **71** [102–104]

Scheme 29.



69 **71** (20–94%) **70**

X = Cl, Br; R = H, Me, Ph; Ar = Ph, 4-MeC_6H_4, 2,4-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 4-$MeOC_6H_4$, 4-FC_6H_4.

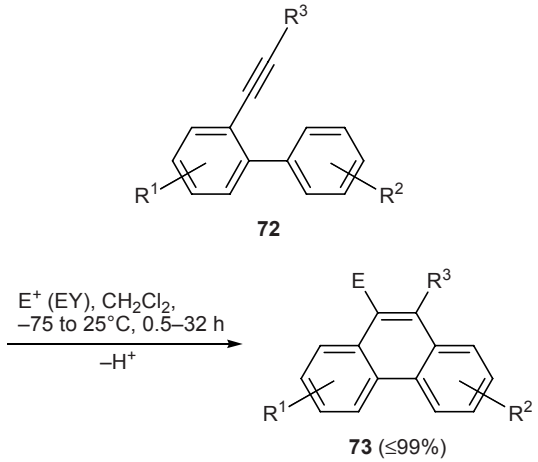
(Scheme 29). In the synthesis of indenes **71** from ketones **69**, the condensation involves two benzene molecules and cationic intermediates generated from the acetylenic compound. These intermediates possess two electrophilic centers: carbonyl carbon atom activated by aluminum halide and vinyl-type cationic center on C^3, the latter appearing as a result of protonation of the C≡C bond [102, 104]. Alcohols **70** lose the hydroxy group by the action of $AlBr_3$, prop-2-yn-1-yl cations thus formed react with benzene, and the subsequent intramolecular alkenylation leads to the formation of indene ring [103, 104].

Availability of a large series of Lewis acids makes it possible to vary experimental alkenylation conditions over a wide range and select appropriate initial compounds (arenes and alkynes), so that target products with a required structure can be obtained. However, the alkenylation is possible only with aromatic compounds possessing sufficiently high π-nucleophilicity, in particular with benzene and its derivatives containing electron-donating alkyl, alkoxy, and hydroxy groups. Presumably, electrophilic activation of alkynes by the action of Lewis acids is not very strong, and the positive charge induced on the acetylenic carbon atoms in intermediates **63** and **64** (Scheme 25) is relatively small.

3.3. Reactions in the Presence of Electrophilic Reagents

Like Lewis acids, addition of an electrophile at a triple bond yields cationic intermediate analogous to **63** or **64**, and these intermediates are capable of reacting with aromatic systems to produce the corresponding alkenylation products. Various compounds, e.g., [Ibpy]BF_4 [105, 106], ICl [107–109], I_2 [108], NBS [108], 4-$O_2NC_6H_4SCl$ [108], and PhSeCl [108], were successfully used as source of electrophilic species in the intramolecular alkenylation of *ortho*-alkynylbiphenyls **72**, which resulted in the formation of phenanthrene structures **73** (Scheme 30). Here, even acetylenic compounds **72** having electron-withdrawing groups (R^3 = 4-XC_6H_4, where X = NO_2, CO_2Et) were reactive [108].

Scheme 30.



72

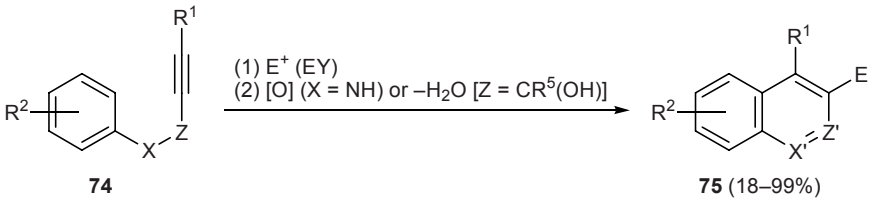
73 (≤99%)

E^+ (EY) = I^+ (IbpyBF_4, ICl, I_2), Br^+ (NBS), 4-$O_2NC_6H_4S^+$ (4-$O_2NC_6H_4SCl$), $PhSe^+$ (PhSeCl); R^1, R^2 = H, MeO, O_2N, CHO, Ph, PhC≡C, 2,3-benzo; R^3 = Bu, Me_3Si, Me_3SiCH_2, 4-XC_6H_4 (X = H, Me, MeO, O_2N, CO_2Et), 2-thienyl.

The same electrophiles were used to obtain substituted quinolines (X′ = N, Z′ = CR^2) [110], naphthalenes (X′ = CR^3, Z′ = CR^4) [111], and 2-naphthols **75** (X′ = CN, Z′ = COH) [111] from the corresponding amines (X = NH, Z = CHR^2), α,β-acetylenic alcohols (X = CHR^3, Z = CR^4OH), and acetylenic ketones **74** (X = CH_2, Z = C=O) (Scheme 31). Analogous intramolecular cyclization of alk-2-yn-1-yl ethers by the action of I_2 or ICl gave substituted 3-iodo-2*H*-benzopyrans [112]. The syntheses of iodo derivatives **73** and **75** (E = I) is especially important, for such compounds can be brought into palladium-catalyzed Sonogashira, Heck–Mizoroki, and Suzuki–Miyaura reactions, carbonylation, intra- and intermolecular cyclizations, etc. [107–112].

2,2,2-Trichloro(bromo)-1,3,2λ^5-benzodioxaphosphole **76** and its substituted derivatives were reported

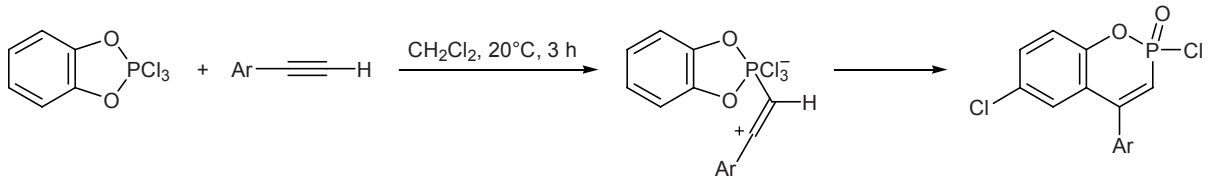
Scheme 31.



74 **75** (18–99%)

E^+ (EY) = I^+ (IbpyBF$_4$, ICl), Br^+ (NBS), $PhSe^+$ (PhSeCl); R^2 = Alk, OAlk, $SiMe_3$, alkenyl, Ar, CO_2Alk; R^2 = H, 4-Me, 3(4)-MeO, 4-F, 4-CO_2Et, 3-O_2N, 3,4-benzo; X = NH, Z = CHR^3 (R^3 = H, Me), X′ = N, Z′ = CHR^2; X = CHR^4 (R^4 = H, Me), Z = CR^5(OH) (R^5 = H, Me), X′ = CR^4, Z′ = CR^5; X = CH_2, Z = CO, X′ = CH, Z′ = C(OH).

Scheme 32.



76 **77** **78** (83–92%

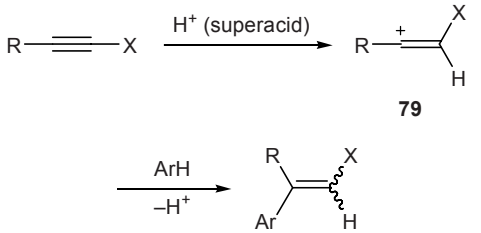
Ar = 4-XC_6H_4 (X = H, Cl, Br).

to act as electrophiles in reactions with terminal aryl- and alkylacetylenes [113–121]. It was presumed that the electrophilic phosphorus atom in molecule **76** adds at the triple C≡C bond to give structure **77** as primary intermediate [113, 114]. The latter undergoes a series of transformations, finally leading to alkenylation products **78** (Scheme 32). The reaction is accompanied by chlorination of the benzene ring in **76**.

3.4. Reactions in Superacids

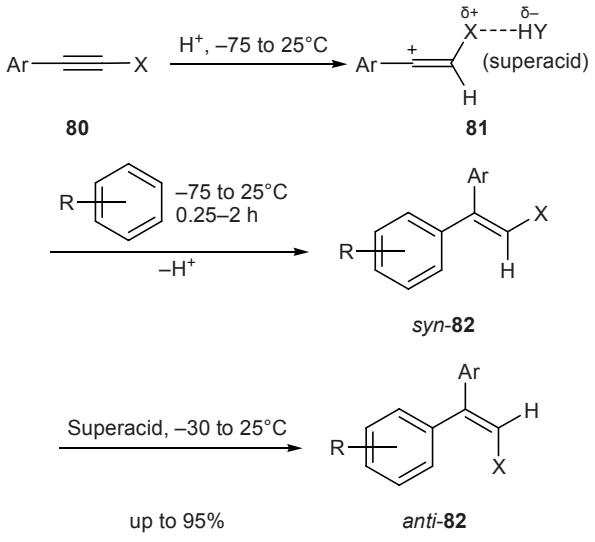
Brønsted superacids like HSO_3F and CF_3SO_3H and conjugated Brønsted–Lewis superacids (HSO_3F–SbF_5, CF_3SO_3H–SbF_5, HF–SbF_5) are characterized by a strong protonating power and weak nucleophilicity and are unique media for generation of cationic species and studying their reactivity [122]. Protonation of triple C≡C bond in superacids give vinyl type cations **79** [123–132] which act as electrophiles toward aromatic π-systems; as a result, the corresponding alkenyl derivatives are formed (Scheme 33).

Scheme 33.



Arylacetylenes **80** containing an electron-withdrawing group X conjugated with the triple bond are converted into cations **81** in superacids [104, 127–133] (Scheme 34). Such cations may be regarded as superelectrophilic species [134] since the electrophilicity (positive charge) on the vinylic carbon atom is enhanced due to the presence of neighboring solvated or

Scheme 34.



X = CO_2H, CO_2Me, CN, COMe, COPh, $COCO_2Et$, $COCF_3$, $PO(OEt)_2$; R^1 = H, Me_n (n = 1–4), $(MeO)_n$ (n = 1,2), OH, 1,2-Cl_2, 1-O_2N-2,4,6-Me_3, 1-SO_2F-2,3,5,6-Me_4, 1-MeCO-2,3,5,6-Me_4, NH_3^+-Me_n (n = 1–4); Ar = $R^2C_6H_n$ [R^2 = H, Me_n (n = 1–5), 4-MeO, 4-F].

completely protonated acceptor group X. Cations **81** effectively react with benzene, alkylbenzenes, methoxy- and hydroxy-substituted arenes, and also with compounds possessing reduced π-nucleophilicity (1,2-dichlorobenzene, 2,4,6-trimethylnitrobenzene, arylammonium ions), and various sterically hindered arenes [130–132]. The primary alkenylation products are kinetically controlled *syn*-adducts **82** which undergo transformation into thermodynamically more stable *anti*-adducts **82** at higher temperature [130–132].

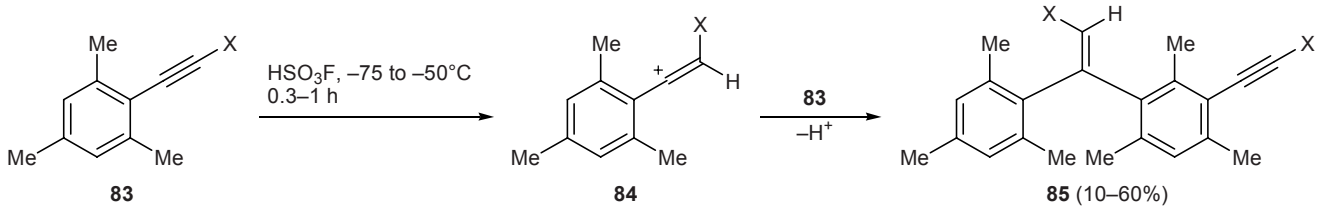
Arylacetylenes **80** in which the aromatic ring contains one to three methyl groups are fairly reactive π-nucleophiles. Provided that no external π-nucleophile is present in the reaction mixture, cations **84** generated from such acetylenes, e.g., from **83**, attack aromatic π-system in initial compound **83** to give dimers **85** [131] (Scheme 35).

Variation of electron-withdrawing power of the substituent X in structures **80** changes π-nucleophilicity of the aromatic ring therein and electrophilicity of cations **81** generated therefrom. For example, compounds **86a** and **86b** react with HSO_3F along different pathways, depending on the nature of the X group. As a result of solvation in superacid (complete protonation), ketone group (X = COMe) [131] becomes a stronger electron acceptor than ester group (X = CO_2Me) [130], and the *para*-tolyl fragment in **86a** (X = COMe) becomes a weaker π-nucleophile than the corresponding fragment in **86b** (X = CO_2Me). On the other hand, cation **87a** is more electrophilic than **87b**. Therefore, cation **87a** does not attack weakly nucleophilic aromatic π-system of initial compound **86a** but reacts with HSO_3F molecule to give fluorosulfonate **88** [131, 135, 136]. By contrast, cation **87b** preferentially reacts with the *para*-tolyl fragment in **86b**, which possesses a sufficient nucleophilicity, yielding dimer **89** [127, 129, 130] (Scheme 36).

If initial acetylenic compound does not contain strong electron-withdrawing groups such as X in structures like **80**, its reaction in superacid cannot be stopped at the stage of formation of monoalkenylation product like **82**. For example, 2-, 3-, and 4-ethynylpyridines react with benzene in CF_3SO_3H to give 1-pyridyl-1,1-diphenylethanes as a result of addition of two benzene molecules to the triple bond in the initial compound [137].

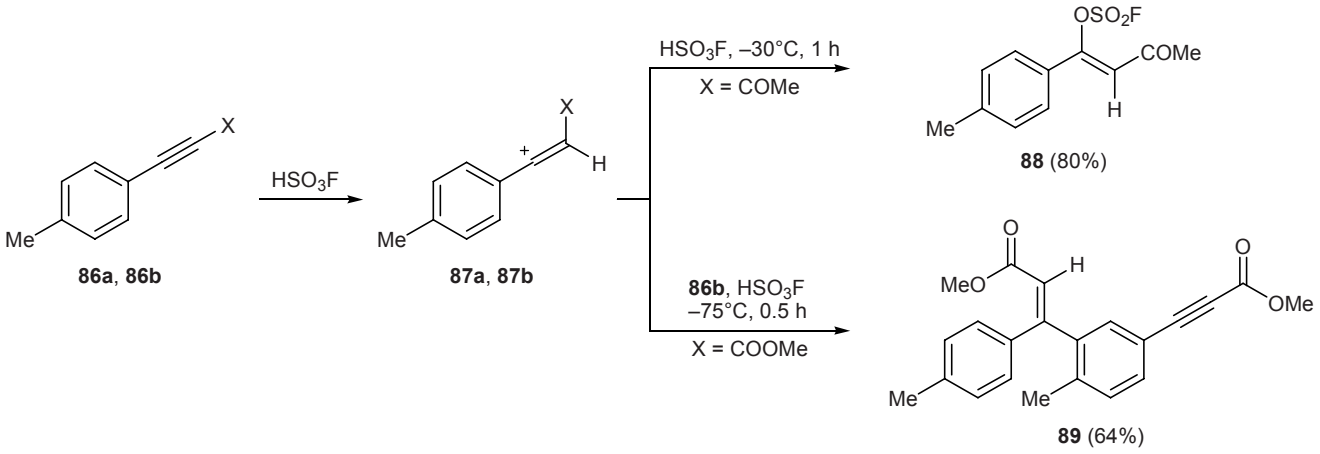
Superacids also promote intramolecular alkenylation. Cyclization of 1,3-diarylprop-2-yn-1-ones **90**

Scheme 35.



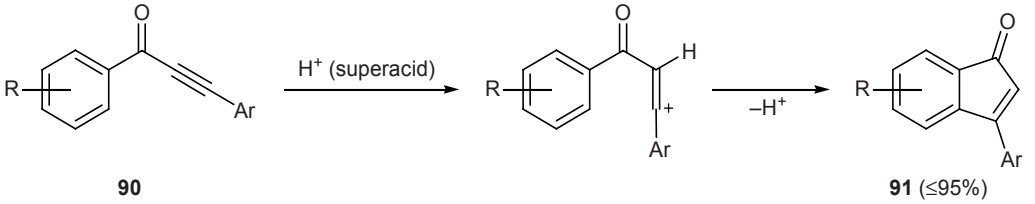
X = COMe, COPh, $PO(OEt)_2$.

Scheme 36.



X = COMe (**a**), CO_2Me (**b**).

Scheme 37.



90 **91** (≤95%)

R = H, Me_n (n = 1, 2), 3-MeO; Ar = 4-XC_6H_4 (X = H, Me, MeO).

leads to 3-arylindenones **91** in nearly quantitative yield [123–126] (Scheme 37). *N*,3-Diphenylprop-2-ynamide is converted into 4-phenylquinolin-2-one via intramolecular ring closure in various superacidic systems [138, 139]. Trifluoromethanesulfonic acid imide promoted transformation of (4-triisopropylsiloxybut-3-yn-1-yl)arenes into 1-triisopropylsiloxydihydronaphthalenes [140, 141].

However, large-scale application of Brønsted superacids (HSO_3F, CF_3SO_3H, etc.) involves serious difficulties related to their utilization. Therefore, extensive studies are performed with the goal of developing more ecologically more friendly alternative superacidic reagents such as strong Lewis acids and solid superacids. Koltunov et al. [138] and Sartori et al. [142] demonstrated the possibility of using zeolites (solid strong acids) to catalyze alkenylation of arenes with acetylenic compounds. This promising line requires further studies.

4. CONCLUSION

One of the most potent methods for the alkenylation of aromatic compounds, Heck–Mizoroki reaction, has been discovered about 40 years ago [9]. Since that time, the set of available methods in organic chemistry was enriched with many new procedures for alkenylation of arenes via reactions with alkenes and alkynes. In the past decade, reactions with acetylenic compounds have been studied especially extensively. These reactions are characterized by high regio- and stereoselectivity, and they ensure preparation of many important but previously inaccessible compounds. At present, studies in this line are becoming a specific field of the chemistry of acetylenic compounds.

REFERENCES

1. Heck, R.F., *Acc. Chem. Res*., 1979, vol. 12, p. 146.
2. Beletskaya, I.P. and Bumagin, N.A., *Russ. J. Org. Chem*., 1996, vol. 32, p. 1715.
3. Beletskaya, I.P. and Cheprakov, A.V., *Chem. Rev*., 2000, vol. 100, p. 3009.
4. Knowles, J.P. and Whiting, A., *Org. Biomol. Chem*., 2007, vol. 5, p. 31.
5. Yin, L. and Liebscher, J., *Chem. Rev*., 2007, vol. 107, p. 133.
6. Nandurkar, N.S. and Bhanage, B.M., *Tetrahedron*, 2008, vol. 64, p. 3655.
7. Diederich, F. and Stang, P.J., *Metal-Catalyzed Cross-Coupling Reactions*, New York: Wiley, 1998.
8. Davis, S.G. and Murahashi, S.I., *Transition Metal Catalyzed Reactions*, Oxford: Blackwell Science, 1999.
9. Li, J.J., *Name Reactions: A Collection of Detailed Reaction Mechanisms*, Berlin: Springer, 2006.
10. Miyaura, N. and Suzuki, A., *Chem. Rev*., 1995, vol. 95, p. 2457.
11. Molander, G.A. and Brown, A.R., *J. Org. Chem*., 2006, vol. 71, p. 9681.
12. Stille, J.K., *Angew. Chem., Int. Ed. Engl*., 1986, vol. 25, p. 508.
13. Santos, L.S., Rosso, G.B., Pilli, R.A., and Eberlin, M.N., *J. Org. Chem*., 2007, vol. 72, p. 5809.
14. Negishi, E., *Acc. Chem. Res*., 1982, vol. 15, p. 340.
15. Ma, S., Ren, H., and Wei, Q., *J. Am. Chem. Soc*., 2003, vol. 125, p. 4817.
16. Gavryushin, A., Kofink, C., Manolikakes, G., and Knochel, P., *Tetrahedron*, 2006, vol. 62, p. 7521.
17. Scheiper, B., Bonnokessel, M., Krause, H., and Furstner, A., *J. Org. Chem*., 2004, vol. 69, p. 3943.
18. Satoh, T., Ogino, Y., and Nakamura, M., *Tetrahedron Lett*., 2004, vol. 45, p. 5785.
19. Satoh, T., Ogino, Y., and Ando, K., *Tetrahedron*, 2005, vol. 61, p. 10262.
20. Satoh, T., Mori, N., and Obuchi, K., *Tetrahedron Lett*., 2007, vol. 48, p. 6453.
21. Heinrich, M.R., Blank, O., Ullrich, D., and Kirschtein, M., *J. Org. Chem*., 2007, vol. 72, p. 9609.
22. Amatore, M., Gosmini, C., and Perichon, J., *Eur. J. Org. Chem*., 2005, p. 989.
23. Lee, P.H., Seomoon, D., and Lee, K., *Org. Lett*., 2005, vol. 7, p. 343.
24. Ritleng, V., Sirlin, C., and Pfeffer, M., *Chem. Rev*., 2002, vol. 102, p. 1731.

25. Alonso, F., Beletskaya, I.P., and Yus, M., *Chem. Rev*., 2004, vol. 104, p. 3079.
26. Nevado, C. and Echavarren, A.M., *Synthesis*, 2005, p. 167.
27. Zeni, G. and Larock, R.C., *Chem. Rev*., 2006, vol. 106, p. 4644.
28. Bandini, M., Emer, E., Tomassi, S., and Umani-Ronchi, A., *Eur. J. Org. Chem*., 2006, p. 3527.
29. Flynn, A.B. and Ogilvie, W.W., *Chem. Rev*., 2007, vol. 107, p. 4698.
30. Soriano, E. and Marco-Contelles, J., *Organometallics*, 2006, vol. 25, p. 4542.
31. Jia, C., Kitamura, T., and Fujiwara, Y., *Acc. Chem. Res*., 2001, vol. 34, p. 633.
32. Jia, C., Lu, W., Oyamada, J., Kitamura, T., Matsuda, K., Irie, M., and Fujiwara, Y., *J. Am. Chem. Soc*., 2000, vol. 122, p. 7252.
33. Jia, C., Piao, D., Oyamada, J., Kitamura, T., and Fujiwara, Y., *J. Org. Chem*., 2000, vol. 65, p. 7516.
34. Jia, C., Piao, D., Oyamada, J., Lu, W., Kitamura, T., and Fujiwara, Y., *Science*, 2000, vol. 287, p. 1992.
35. Kitamura, T., Yamamoto, K., Kotani, M., Kitamura, T., Jia, C., and Fujiwara, Y., *Bull. Chem. Soc. Jpn*., 2003, vol. 76, p. 1889.
36. Li, K., Zeng, Y., Neuenswander, B., and Tung, J.A., *J. Org. Chem*., 2005, vol. 70, p. 6515.
37. Tunge, J.A. and Foresee, L.N., *Organometallics*, 2005, vol. 24, p. 6440.
38. Trost, B.M., Toste, F.D., and Greenman, K., *J. Am. Chem. Soc*., 2003, vol. 125, p. 4518.
39. Oyamada, J., Lu, W., and Kitamura, T., *Tetrahedron*, 2006, vol. 62, p. 6918.
40. Ueura, K., Satoh, T., and Miura, M., *Org. Lett*., 2007, vol. 9, p. 1407.
41. Ueura, K., Satoh, T., and Miura, M., *J. Org. Chem*., 2007, vol. 72, p. 5362.
42. Hong, P., Cho, B.-R., and Yamazaki, H., *Chem. Lett*., 1979, p. 339.
43. Lim, Y.-G., Lee, K.-H., Koo, B.T., and Kang, J.-B., *Tetrahedron Lett*., 2001, vol. 42, p. 7609.
44. Lim, Y.-G., Lee, K.-H., Moon, C.W., Hong, J.-B., and Jun, C.-H., *Org. Lett*., 2003, vol. 5, p. 2759.
45. Kakiuchi, F. and Murai, S., *Acc. Chem. Res*., 2002, vol. 35, p. 826.
46. Murakami, M. and Hori, S., *J. Am. Chem. Soc*., 2003, vol. 125, p. 4720.
47. Nakao, Y., Kanyiva, K.S., and Hiyama, T., *J. Am. Chem. Soc*., 2008, vol. 130, p. 2448.
48. Cacchi, S., Fabrizi, G., Marinelli, F., Moro, L., and Pace, P., *Tetrahedron*, 1996, vol. 52, p. 10225.
49. Ahlquist, M., Fabrizi, G., Cacchi, S., and Norrby, P.-O., *J. Am. Chem. Soc*., 2006, vol. 128, p. 12785.
50. Arcadi, A., Cacchi, S., Fabrizi, G., Marinelli, F., and Pace, P., *Eur. J. Org. Chem*., 2000, p. 4099.
51. Cheng, Y., Duan, Z., Yu, L., Li, Z., Zhy, Y., and Wu, Y., *Org. Lett*., 2008, vol. 10, p. 901.
52. Shintani, R., Yamagami, T., and Hayashi, T., *Org. Lett*., 2006, vol. 8, p. 4799.
53. Donets, P.A. and van der Eycken, E.V., *Org. Lett*., 2007, vol. 9, p. 3017.
54. Liu, J., Shen, M., Zhang, Y., Li, G., Khodabocus, A., Rodriguez, S., Qu, B., Farina, V., Senanayake, C.H., and Lu, B.Z., *Org. Lett*., 2006, vol. 8, p. 3573.
55. Larock, R.C., Yum, E.K., Doty, M.J., and Sham, K.K., *J. Org. Chem*., 1995, vol. 60, p. 3270.
56. Larock, R.C., Yum, E.K., and Refvik, M.D., *J. Org. Chem*., 1998, vol. 63, p. 7652.
57. Kadnikov, D.V. and Larock, R.C., *J. Org. Chem*., 2004, vol. 69, p. 6772.
58. Roesch, K.R. and Larock, R.C., *J. Org. Chem*., 1998, vol. 63, p. 5306.
59. Kadnikov, D.V. and Larock, R.C., *J. Org. Chem*., 2003, vol. 68, p. 9423.
60. Zhang, H. and Larock, R.C., *J. Org. Chem*., 2003, vol. 68, p. 5132.
61. Larock, R.C. and Doty, M.J., *J. Org. Chem*., 1993, vol. 58, p. 4579.
62. Quan, L.G., Gevorgyan, V., and Yamamoto, Y., *J. Am. Chem. Soc*., 1999, vol. 121, p. 3545.
63. Chang, K.-J., Rayabarapu, D.K., and Cheng, C.-H., *J. Org. Chem*., 2004, vol. 69, p. 4781.
64. Vicente, J., Abad, J.-A., and Gil-Rubio, J., *Organometallics*, 1996, vol. 15, p. 3509.
65. Deng, R., Sun, L., and Li, Z., *Org. Lett*., 2007, vol. 9, p. 5207.
66. Nakao, Y., Oda, S., Yada, A., and Hiyama, T., *Tetrahedron*, 2006, vol. 62, p. 7567.
67. Nakao, Y., Kanyiva, K.S., Oda, S., and Hiyama, T., *J. Am. Chem. Soc*., 2006, vol. 128, p. 8146.
68. Nakao, Y., Yada, A., Ebata, S., and Hiyama, T., *J. Am. Chem. Soc*., 2007, vol. 129, p. 2428.
69. Hayashi, T., Inoue, K., Taniguchi, N., and Ogasawara, M., *J. Am. Chem. Soc*., 2001, vol. 123, p. 9918.
70. Kim, N., Kim, K.S., Gupta, A.K., and Oh, C.H., *Chem. Commun*., 2004, p. 618.
71. Zeng, H. and Hua, R., *J. Org. Chem*., 2008, vol. 73, p. 558.
72. Kurahashi, T., Shinokubo, H., and Osuka, A., *Chem. Commun*., 2006, p. 6336.
73. Tsukamoto, H. and Kondo, Y., *Org. Lett*., 2007, vol. 9, p. 4227.
74. Cacchi, S., Fabrizi, G., Goggiamani, A., and Persiani, D., *Org. Lett*., 2008, vol. 10, p. 1597.
75. Shi, Y., Peterson, S.M., Haberaecker, W.W., and Blum, S.A., *J. Am. Chem. Soc*., 2008, vol. 130, p. 2168.

76. Terao, Y., Nomoto, M., Satoh, T., Miura, M., and Nomura, M., *J. Org. Chem*., 2004, vol. 69, p. 6942.
77. Yamashita, F., Kuniyashi, H., Terao, Y., and Kambe, N., *Org. Lett*., 2008, vol. 10, p. 101.
78. Yamaguchi, M., Hayashi, A., and Hirama, M., *J. Am. Chem. Soc*., 1995, vol. 117, p. 1151.
79. Yamaguchi, M., Arisawa, M., Omata, K., Kabuto, K., Hirama, M., and Uchimaru, T., *J. Org. Chem*., 1998, vol. 63, p. 7298.
80. Kido, Y., Yoshimura, S., Yamaguchi, M., and Uchimaru, T., *Bull. Chem. Soc. Jpn*., 1999, vol. 72, p. 1445.
81. Amemiya, R. and Yamaguchi, M., *Eur. J. Org. Chem*., 2005, p. 5145.
82. Kido, Y., Yonehara, F., and Yamaguchi, M., *Tetrahedron*, 2001, vol. 57, p. 827.
83. Li, R., Wang, S.R., and Lu, W., *Org. Lett*., 2007, vol. 9, p. 2219.
84. Oyamada, J. and Kitamura, T., *Tetrahedron*, 2007, vol. 63, p. 12754.
85. Pastine, S.J., Youn, S.W., and Sames, D., *Tetrahedron*, 2003, vol. 59, p. 8859.
86. Pastine, S.J., Youn, S.W., and Sames, D., *Org. Lett*., 2003, vol. 5, p. 1055.
87. Kenny, R.S., Mashelkar, U.C., Rane, D.M., and Bezawada, D.K., *Tetrahedron*, 2006, vol. 62, p. 9280.
88. Pastine, S.J. and Sames, D., *Org. Lett*., 2003, vol. 5, p. 4053.
89. Zhang, Y., *Tetrahedron*, 2006, vol. 62, p. 3917.
90. Shen, H.C., *Tetrahedron*, 2008, vol. 64, p. 3885.
91. Jimenez-Nunez, E. and Echavarren, A.M., *Chem. Commun*., 2007, p. 333.
92. Hashmi, A.S.K., *Chem. Rev*., 2007, vol. 107, p. 3180.
93. Reetz, M.T. and Sommer, K., *Eur. J. Org. Chem*., 2003, p. 3485.
94. Shi, Z. and He, C., *J. Org. Chem*., 2004, vol. 69, p. 3669.
95. Marion, N., Diez-Gonzalez, S., Fremont, P., Noble, A.R., and Nolan, S.P., *Angew. Chem., Int. Ed*., 2006, vol. 45, p. 3647.
96. Hashmi, A.S.K. and Blanko, M.C., *Eur. J. Org. Chem*., 2006, p. 4340.
97. Ferrer, C. and Echavarren, A.M., *Angew. Chem., Int. Ed*., 2006, vol. 45, p. 1105.
98. Tsuchimoto, T., Maeda, T., Shirakawa, E., and Kawakami, Y., *Chem. Commun*., 2000, p. 1573.
99. Song, C.E., Jung, D., Choung, S.Y., Roh, E.J., and Lee, S., *Angew. Chem., Int. Ed*., 2004, vol. 43, p. 6183.
100. Choi, D.S., Kim, J.H., Shin, U.S., Deshmukh, R.R., and Song, C.E., *Chem. Commun*., 2007, p. 3482.
101. Otani, T., Kunimatsu, S., Nihei, H., Abe, Y., and Saito, T., *Org. Lett*., 2007, vol. 9, p. 5513.
102. Vasil'ev, A.V. and Shchukin, A.O., *Russ. J. Org. Chem*., 2006, vol. 42, p. 1239.
103. Shchukin, A.O. and Vasil'ev, A.V., *Russ. J. Org. Chem*., 2007, vol. 43, p. 784.
104. Shchukin, A.O. and Vasilyev, A.V., *Appl. Catal., A*, 2008, vol. 336, p. 140.
105. Goldfinger, M.B. and Swager, T.S., *J. Am. Chem. Soc*., 1994, vol. 116, p. 7895.
106. Goldfinger, M.B., Crawford, K.B., and Swager, T.S., *J. Am. Chem. Soc*., 1997, vol. 119, p. 4578.
107. Yao, T., Campo, M.A., and Larock, R.C., *Org. Lett*., 2004, vol. 6, p. 2677.
108. Yao, T., Campo, M.A., and Larock, R.C., *J. Org. Chem*., 2005, vol. 70, p. 3511.
109. Li, C.-W., Wang, C.-I., Liao, H.-Y., Chaudhuri, R., and Liu, R.-S., *J. Org. Chem*., 2007, vol. 72, p. 9203.
110. Zhang, X., Campo, M.A., Yao, T., and Larock, R.C., *Org. Lett*., 2005, vol. 7, p. 763.
111. Zhang, X., Sarkar, S., and Larock, R.C., *J. Org. Chem*., 2006, vol. 71, p. 236.
112. Worlikar, S.A., Kesharwani, T., Yao, T., and Larock, R.C., *J. Org. Chem*., 2007, vol. 72, p. 1347.
113. Mironov, V.F., Konovalov, A.I., Litvinov, I.A., Gubaidullin, A.T., Petrov, R.R., Shtyrlina, A.A., Zyablikova, T.A., Musin, R.Z., Azancheev, N.M., and Il'yasov, A.V., *Russ. J. Gen. Chem*., 1998, vol. 68, p. 1414.
114. Mironov, V.F., Litvinov, I.A., Shtyrlina, A.A., Gubaidullin, A.T., Petrov, R.R., Konovalov, A.I., Azancheev, N.M., and Musin, R.Z., *Russ. J. Gen. Chem*., 2000, vol. 70, p. 1046.
115. Mironov, V.F., Petrov, R.R., Shtyrlina, A.A., Gubaidullin, A.T., Litvinov, I.A., Musin, R.Z., and Konovalov, A.I., *Russ. J. Gen. Chem*., 2001, vol. 71, p. 67.
116. Mironov, V.F., Shtyrlina, A.A., Gubaidullin, A.T., Bogdanov, A.V., Litvinov, I.A., Azancheev, N.M., Latypov, Sh.K., Musin, R.Z., and Efremov, Yu.Ya., *Izv. Ross. Akad. Nauk, Ser. Khim*., 2004, p. 186.
117. Mironov, V.F., Shtyrlina, A.A., Varaksina, E.N., Efremov, Yu.Ya., and Konovalov, A.I., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1798.
118. Mironov, V.F., Sergeenko, G.G., Bauer, I., and Habicher, W.-D., *Russ. J. Org. Chem*., 2006, vol. 42, p. 1453.
119. Nemtarev, A.V., Varaksina, E.N., Mironov, V.F., Musin, R.Z., and Konovalov, A.I., *Russ. J. Org. Chem*., 2007, vol. 43, p. 468.
120. Nemtarev, A.V., Varaksina, E.N., Mironov, V.F., Musin, R.Z., and Konovalov, A.I., *Russ. J. Org. Chem*., 2007, vol. 43, p. 1737.
121. Nemtarev, A.V., Varaksina, E.N., Mironov, V.F., and Konovalov, A.I., *Russ. J. Org. Chem*., 2004, vol. 40, p. 296.
122. Olah, G.A., Prakash, G.K.S., and Sommer, J., *Superacids*, New York: Wiley, 1985.
123. Vasilyev, A.V., Walspurger, S., Pale, P., and Sommer, J., *Tetrahedron Lett*., 2004, vol. 45, p. 3379.

124. Vasilyev, A.V., Walspurger, S., Haouas, M., Sommer, J., Pale, P., and Rudenko, A.P., *Org. Biomol. Chem*., 2004, vol. 2, p. 3483.

125. Vasil'ev, A.V., Walspurger, S., Pale, P., Sommer, J., Haouas, M., and Rudenko, A.P., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1769.

126. Walspurger, S., Vasilyev, A.V., Sommer, J., and Pale, P., *Tetrahedron*, 2005, vol. 61, p. 3559.

127. Savechenkov, P.Yu., Rudenko, A.P., and Vasil'ev, A.V., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1065.

128. Rudenko, A.P., Savechenkov, P.Yu., and Vasil'ev, A.V., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1377.

129. Savechenkov, P.Yu., Rudenko, A.P., and Vasil'ev, A.V., *Russ. J. Org. Chem*., 2004, vol. 40, p. 1633.

130. Savechenkov, P.Yu., Rudenko, A.P., Vasil'ev, A.V., and Fukin, G.K., *Russ. J. Org. Chem*., 2005, vol. 41, p. 1316.

131. Aristov, S.A., Vasil'ev, A.V., Fukin, G.K., and Rudenko, A.P., *Russ. J. Org. Chem*., 2007, vol. 43, p. 691.

132. Shchukin, A.O., Vasil'ev, A.V., Aristov, S.A., Fukin, G.K., and Rudenko, A.P., *Russ. J. Org. Chem*., 2008, vol. 44, p. 965.

133. Rendy, R., Zhang, Y., McElrea, A., Gomez, A., and Klumpp, D.A., *J. Org. Chem*., 2004, vol. 69, p. 2340.

134. Olah, G.A. and Klumpp, D.A., *Acc. Chem. Res*., 2004, vol. 37, p. 211.

135. Walspurger, S., Vasil'ev, A.V., Sommer, J., Pale, P., Savechenkov, P.Yu., and Rudenko, A.P., *Russ. J. Org. Chem*., 2005, vol. 41, p. 1485.

136. Vasilyev, A.V., Walspurger, S., Chassaing, S., Pale, P., and Sommer, J., *Eur. J. Org. Chem*., 2007, p. 5740.

137. Klumpp, D.A., Rendy, R., Zhang, Y., McElrea, A., Gomez, A., and Dang, H., *J. Org. Chem*., 2004, vol. 69, p. 8108.

138. Koltunov, K.Yu., Walspurger, S., and Sommer, J., *Chem. Commun*., 2004, p. 1754.

139. Koltunov, K.Yu., Walspurger, S., and Sommer, J., *Eur. J. Org. Chem*., 2004, p. 4039.

140. Zhang, L. and Kozmin, S.A., *J. Am. Chem. Soc*., 2004, vol. 126, p. 10204.

141. Zhang, L., Sun, J., and Kozmin, S.A., *Tetrahedron*, 2006, vol. 62, p. 11371.

142. Sartori, G., Bigi, F., Pastorio, A., Porta, C., Arienti, A., Maggi, R., Moretti, N., and Gnappi, G., *Tetrahedron Lett*., 1995, vol. 36, p. 9177.