Russian Chemical Reviews **76** (6) 507 – 527 (2007) © 2007 Russian Academy of Sciences and Turpion Ltd

DOI 10.1070/RC2007v076n06ABEH003712

Acetylene: new prospects of classical reactions

B A Trofimov, N K Gusarova

Contents

I.	Introduction	507
II.	Acetylene reactions in superbasic media	508
III.	Chemistry of acetylenic hydroxy acids and their derivatives	514
IV.	Acetylene- and allene-derived carbanions	515
V.	New reactions involving pyrrole	516
VI.	The use of acetylenes in the synthesis of phosphines and phosphine chalcogenides	517
VII.	Acetylene derivatives of silicon and germanium	519
VIII.	New acetylene-based technologies	520
IX.	Conclusion	521

Abstract. The latest results in the field of classical reactions of acetylene are analysed. Attention is focused on reactions catalysed by strong bases (vinylation, alkynol synthesis, acetylene – allene isomerisation) and related syntheses. The bibliography includes 347 references.

I. Introduction

Chemistry of acetylene, a versatile building block of the organic synthesis, is continued to be rapidly developed.[1] As compared with ethylene, highly reactive acetylene and its derivatives better match the trends in the development of chemical industry, which is more and more oriented to the production of science intensive chemicals for modern technologies, medicine and agriculture. Acetylene can be considered as an accumulator of high-density energy, *i.e.*, the heat consumed in its formation is liberated in chemical reactions thus promoting them and providing the shortest and the least power-consuming way to the target products.

Although quite recently, acelylene was virtually beyond competition as the basic chemical used in the industry, now it has lost its leading position. At the same time, according to certain analysts, acetylene might again become the leader.[2–7] Future will show whether or not this happens and to the full extent or only partly, however, there are objective prerequisites for this to happen.

Acetylene is mainly produced from oil and natural gas by oxidative pyrolysis in an electric discharge, in plasma, by laser technologies and using solar energy. Moreover, acetylene is the main side product in the ethylene synthesis.[2] At the same time, acetylene can also be produced from coal. Accounts of natural energy resources show that oil and natural gas fields are being rapidly exhausted, while the coal resources may last for centuries. Hence, the return to coal-based technologies seems quite likely.[2,5,6] Acetylene is obtained from coal by both the traditional carbide method and the modern plasma technologies as well as by hydrogenation, gasification or *via* the synthesis gas. Moreover, different types of biomass such as lignine and various carbon-containing industrial and domestic waste may be transformed into acetylene by their fast pyrolysis in plasma. The latter method seems especially attractive, being associated with the solution of environmental problems.

Long-term economical prognoses allow one to assume that new, constantly modernised plasma technologies for the production of acetylene from coal have a sufficient potential for making acetylene once again the chief chemical in the manufacturing of commercial products such as vinyl chloride, vinyl acetate, acrylates, chloroprene and chlorinated solvents.[2,5–7]

To make the quest for new synthetic approaches to the chemistry of acetylene more effective, the theoretical studies based on high-level *ab initio* quantum-chemical calculations are invoked with increasing frequency.[8,9]

Among the popular synthetic methods actively elaborated today, classical reactions of the addition of nucleophiles to the triple bond, the acetylene – allene – diene isomerisation and the transformations of acetylene and allene-derived carbanions deserve mention. Recent reviews[10,11] show numerous examples of syntheses of heterocyclic and carbocyclic compounds by the addition of different nucleophiles to acetylenes.

The quest for new reactions of the formation of C–C bonds that involve acetylene-derived carbanions (metal acetylenides) and especially those based on the addition of acetylene to the carbonyl group (the Favorsky alkynol synthesis and its analogues) is carried on.[12] Numerous studies on transition metal acetylenides were summarised in several reviews.[13,14]

Unconventional prospects for the organic synthesis are opened up by acetylenic sugars, which were the subject of hundreds of publications (*e.g.*, for a review, see Ref. 15).

The progressively greater efforts are directed to the quest for new organic semiconductors and optoelectronic materials based on acetylene polymers and oligomers. Today, high expectations are placed on polyarylene ethynylenes, *i.e.*, polymers containing alternating triple bonds and arene

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Received 3 April 2007
Uspekhi Khimii **76** (6) 550 – 570 (2007); translated by T Ya Safonova

groups,[16–19] and unique polyyne structures, which can be synthesised through alkylidenecarbenes and -carbenoids.[20,21] The interest in polyynes[22,23] and arylene–ethynylene systems[24] is explained by their prospects as the molecular wires and also in the context of studies of carbyne and its analogues as the allotropic forms of carbon.

The appearance of new synthetic approaches to the design of new acetylenic structures, which are based on cross-coupling reactions catalysed by transition metal complexes, has revolutionised the assembling of different acetylene-containing systems and ensembles.[25–27]

In the recent decades, systematic studies were carried out aimed at further development of classical reactions of acetylene with the use of superbasic catalysts and reagents. The present review is devoted to the brief analysis of achievements in this field. At the same time, due to the limited volume, it chiefly deals with the addition reactions to the triple bond (vinylation), addition of acetylene-derived carbanions (alkynol synthesis) and acetylene–allene–diene isomerisation, which serve as the basis for the most popular synthetic methods in the acetylene chemistry and are used most widely in laboratories and the industry.

The elaboration of a new approach to the enhancement of the reactivity of nucleophilic reagents, which is associated with the use of superbasic catalysts, have led not only to the refining of most important base-catalysed reactions of acetylene but also to the discovery of new reactions involving the triple bond and the development of synthetic methods based on them.[7,28–43]

II. Acetylene reactions in superbasic media

The concept of superbasicity was first formulated by Trofimov[44] in 1977: 'a medium consisting of a strong base and a solvent or a reagent that specifically binds cations thus 'stripping' the conjugated anions is considered superbasic...'. Later, this concept was systematically used in the refinement of classical reactions involving triple carbon–carbon bonds (Refs 7, 28–30, 33, 41 and 43).

Obviously, within the framework of this concept, the definition of superbasicity is the 'mirror image' of superacidity, *i.e.*, a superbase is a complex of a strongly ionised base (the Brønsted base) with a ligand that can specifically interact with the cation of this base (the Lewis base) in a medium capable of weak solvation of anions (as a rule, in a medium of a polar hydroxyl-free solvent).[33,41]

$$\underset{\text{Brønsted base}}{M^+B^-} + \underset{\text{Lewis base}}{Y} \rightleftharpoons \underset{\text{Superbase}}{B^-[MY]^+}$$

M = Li, Na, K, Rb, Cs; B is a carbanion, H, OH, OR, NH_2, NR_2; Y correspond to ethers (polyethers), amines (polyamines), NH_3, cryptands, sulfoxides, sulfones, amides, phosphine oxides, *etc.*

Systems with the Hammett acidity function (H_-) higher than 18.5, *i.e.*, the systems with the basicity unattainable in hyroxyl-containing solvents (water and alcohols) due to the limitations imposed by the intrinsic acidity of the medium, were assigned[33,41] to superbases.

Among diverse superbasic systems, the system KOH–DMSO proved to be the most suitable for the systematic application in the acetylene chemistry as the simplest, most easily prepared and versatile system.[7,28–30,32,33,41–46] Its upper basicity limit is determined by the DMSO acidity ($pK_a = 35.1$); however, the acidity does not usually exceed 32 (in the H_- scale) unless special measures have been undertaken for the removal of water liberated in the formation of dimsyl potassium.

$$KOH + Me_2SO \rightleftharpoons \overset{+}{K}\overset{-}{C}H_2S(O)Me + H_2O.$$

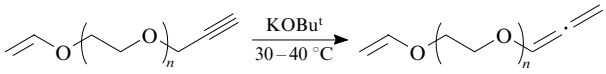
A great advantage of the system KOH–DMSO is its controllable basicity. As the water content in DMSO decreases to 25%, the system passes to the superbasicity region ($H_- > 20$). With further decrease in the water concentration, the value of H_- sharply increases approaching 30–32 for 99% DMSO.[41]

Yet another advantage of the system KOH–DMSO is its ability for autostabilisation (self-adjustment), *i.e.*, its basicity is maintained on a constant level due to the absorption of water (if water is liberated in the reaction) by the solid phase (KOH); the KOH concentration in the liquid phase is low ($\sim$0.04 mol litre^{-1} in pure DMSO) and the consumed KOH is replenished from the solid phase, *i.e.*, its concentration is automatically kept constant. Thus, the reactions in this system often acquire the features of the phase-transfer catalysis.[41]

1. Development of classical acetylene reactions

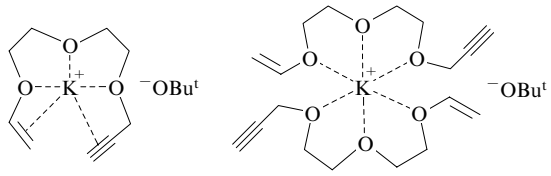
a. The Favorsky acetylene–allene isomerisation

The selective isomerisation of propargyl ethers to allenyl ethers was first carried out under the action of $KOBu^t$ on propargyl vinyl ethers of ethylene glycol oligomers.[47,48]

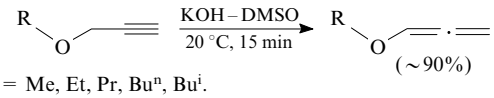


$n = 1–3$.

The superbasicity of the reaction mixture was achieved due to the formation of chelate complexes of potassium cations with the polyether chain.



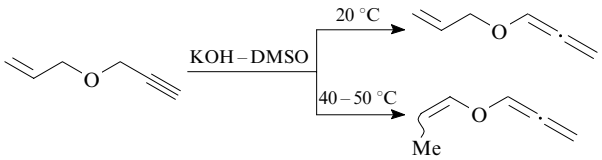
The use of the superbasic system KOH–DMSO in the isomerisation of propargyl ethers have led to the development of an efficient and highly selective method for the synthesis of alkyl allenyl ethers.[49]



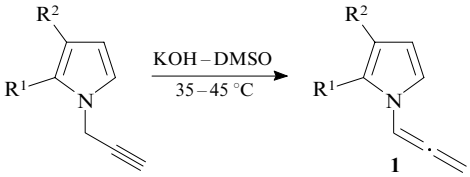
R = Me, Et, Pr, Bu^n, Bu^i.

This reaction made accessible the alkyl allenyl ethers, which so far pertained to the insufficiently explored class of substances.[7,50–52] Obviously, their synthetic potential as the reactive monomers and building blocks is more multifaceted as compared with the corresponding vinyl ethers that have found wide application in both the organic synthesis[2,28,53–58] and polymer chemistry.[59–67]

It was shown that the system KOH–DMSO allows one to selectively isomerise the propargyl group of an allyl propargyl ether to the allenyl group, leaving intact the allyl fragment. When carried out at higher temperatures, this reaction can shift the double bond to afford allenyl prop-1-enyl ether.[41]

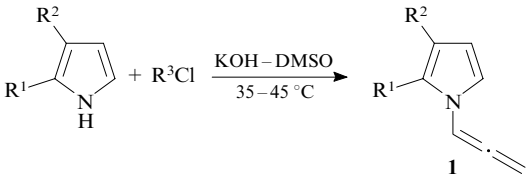


N-Allenylpyrroles **1**, the promising monomers[68] and building blocks in synthetic chemistry, which were difficult to synthesise until recently, were easily obtained in high yields by the isomerisation of *N*-propargylpyrroles catalysed by the system KOH – DMSO.[69]



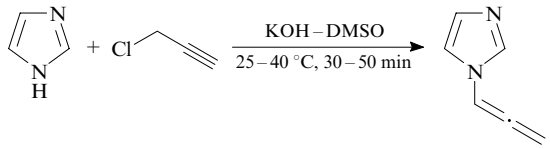
R^1	R^2	Yield of **1** (%)	R^1	R^2	Yield of **1** (%)
H	H	63	Me	Me	49
Me	H	68	$(CH_2)_4$		88
Ph	H	70			

N-Allenylpyrroles **1** can be synthesised in a one-pot procedure using both propargyl chloride[70] (which is sufficiently obvious) and much cheaper 2,3-dichloroprop-1-ene[71] and 1,2,3-trichloropropane,[72] which are the side products of the industrial synthesis of epichlorohydrin. In this case, the system KOH – DMSO serves not only as the catalyst, but also as the reagent and, hence, should be taken in a superstoichiometric amount.

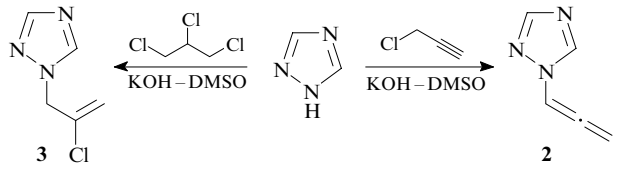


R^1 = H, Me, Ph; R^2 = H, Me; $R^1 - R^2$ = $(CH_2)_4$;
R^3 = $CH_2C{\equiv}CH$, $CH_2CCl{=}CH_2$, $CH_2CHClCH_2Cl$.

The same superbase and the same reagents allowed the one-pot allenylation of other azoles to be carried out.[73, 74] For example, *N*-allenylimidazole was synthesised from imidazole and propargyl chloride in the yield of 75%.



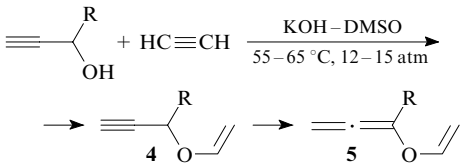
1,2,4-Triazole behaves in a similar way, namely, its reaction with propargyl chloride produces *N*-allenyl-1,2,4-triazole (**2**) in the yield of 31%.[73, 74] The use of trichloropropane in allenylation allows one to stop the reaction after the formation of *N*-chloroallyl derivative **3** (yield 21%).[73]



b. Nucleophilic addition to a triple bond (vinylation)

Superbasic catalysts have extended in principle the potentials of the classical Favorsky reaction of vinylation.[75] For example, vinylation of acetylenic alcohols with acetylene is impossible in the presence of common bases (alkali metal hydroxides or alkoxides); however, in superbasic systems such as KOH – DMSO this reaction proceeds sufficiently smoothly.[41]

As a rule, it is rather difficult to stop this reaction in a stage of the formation of a vinyl ether of acetylenic alcohol **4** (this requires special measures to be undertaken). Usually, the acetylene – allene isomerisation proceeds simultaneously to afford the corresponding allenyl vinyl ethers **5** (yields up to 80%).[76, 77]



R = H, Me, Et, Pr^n, Pr^i, Bu^t.

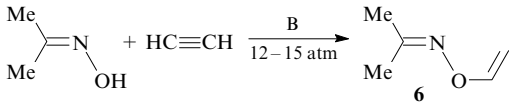
This reaction is the most promising for the transformation of commercially available propargyl alcohol into vinyloxyallene.

A new generation of superbases, the catalytic systems CsF – MOH – DMSO (M = Li, Na, K) have been developed recently. As a rule, they are more active[41, 78 – 83] than the system KOH – DMSO. In a simple way, their enhanced activity can be explained by the formation of caesium hydroxide (a base stronger than potassium hydroxide) due to the shift of the equilibrium to the formation of poorly soluble fluorides, particularly, lithium fluoride.[41]

$$CsF + MOH \rightleftharpoons CsOH + MF$$

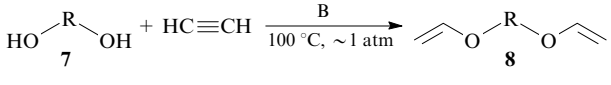
M = Li, Na, K.

A comparison of the activity of two superbasic catalytic systems, namely, KOH – DMSO and CsF – NaOH – DMSO, in the vinylation of acetone oxime shows that the caesium system is much more active. In the presence of this system, the optimum reaction temperature was lower (by ~10 °C) and the yield of *O*-vinyl acetone oxime (**6**) was higher (by 20%)[78, 80] as compared with the system KOH – DMSO.



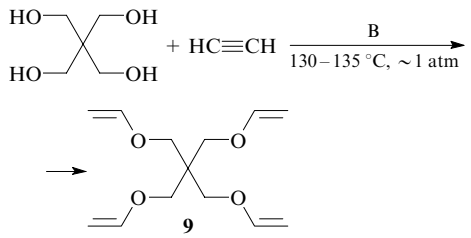
B	*T* /°C	Yield of **6** (%)
CsF – NaOH – DMSO	70 – 72	85
KOH – DMSO	78 – 80	65

Yet more impressive difference in the activities of these two superbasic catalytic systems was observed in the vinylation of polyhydric alcohols. Thus the vinylation of glycols **7** at 100 °C and atmospheric pressure in the presence of the system CsF – NaOH – DMSO afforded divinyl ethers **8** in the yields from 45% to 90% (depending on the glycol structure), whereas in the KOH – DMSO system, the yield of divinyl ethers was at the level of 10%.[41, 83]



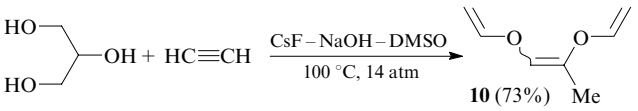
R = $(CH_2)_3$, $(CH_2)_4$, $MeCH(CH_2)_2$, $(CH_2)_7$;
B = CsF – NaOH – DMSO, KOH – DMSO.

In the reaction of acetylene with pentaerythritol carried out at 130 – 135 °C and the atmospheric pressure in the system CsF – NaOH – DMSO, the yield of tetravinyl ether of pentaerythritol (**9**) exceeded 60%, whereas in the system KOH – DMSO, its yield was 5%.[41]

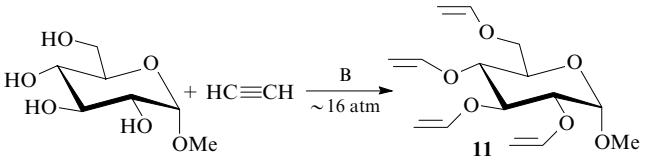


B = CsF – NaOH – DMSO, KOH – DMSO.

The reaction of glycerol with acetylene in the system CsF – NaOH – DMSO produced 1,2-bis(vinyloxy)prop-1-ene (**10**) rather than the expected trivinyl ether of glycerol.[81] Thus, this reaction represents a new type of vinylation, namely, the eliminative vinylation.[84] In the presence of the system KOH – DMSO as the catalyst, only traces of compound **10** were obtained.

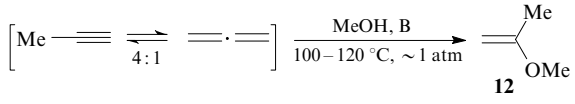


Recently, tetravinyl ether **11** was synthesised from methyl α-D-glucoside in the presence of superbasic catalysts KOH – DMSO and KOH – THF.[85]



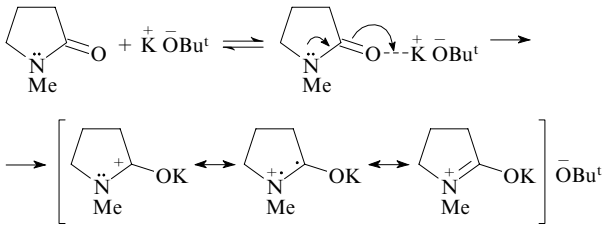
B	T /°C	t /h	Yield of **11** (%)
KOH – DMSO	85 – 87	1	75
KOH – THF	135 – 140	6	52

Superbasic catalytic systems that allow one to perform isopropenylation of methanol with methylacetylene (the second most readily accessible acetylenic hydrocarbon) at the atmospheric pressure and 100 – 120 °C have been developed.[86] This made it possible to synthesise[86] 2-methoxyprop-1-ene (**12**), a valuable monomer and reagent, which has found its application in the industrial syntheses of fragrant compounds, vitamins and carotenoids.[87–90] Complexes of potassium and caesium *tert*-alkoxides with *N*-methylpyrrolidone (NMP) proved to be the most active in this reaction.

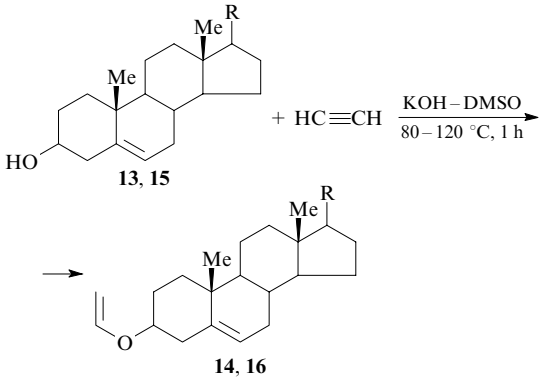


B = KOBu^t – NMP (the yield of compound **12** is 87 %), $CsOCMe_2Et$ – NMP (87%), KOH – DMSO (60%), CsOMe – NMP (22%), CsF – NaOH – NMP (11%), $2\,KOH \cdot H_2O$ – NMP (6%).

Apparently, this is associated with the formation of a charge-transfer complex between NMP and alkoxides. This is evidenced by the presence of the charge transfer bands (283, 543, 580 nm; bright purple colour) in the UV spectrum of a KOBu^t solution in NMP and also by the high-frequency shift of vibrations of the C=O group (1683 $cm^{-1} \rightarrow 1693$ cm^{-1}, probably due to the contribution of the vibrations of the $^+N{=}C$ group) observed in the IR spectrum.[41]

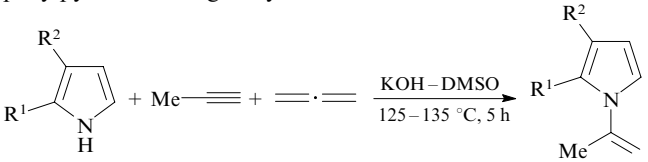


At present, the superbasic catalytic system KOH – DMSO is the most versatile for the vinylation reactions.[7,41,43] Thus this allowed the vinylation of cholesterol **13** to be carried out under mild conditions (without epimerisation and migration of the double bond) to afford the quantitative yield of optically active liquid-crystalline vinyl ether **14**, which is used as a monomer and a highly reactive intermediate in the synthesis of new compounds of the steroid series.[91] In the presence of the same catalytic pair, pregnenolone **15** and acetylene gave vinyl ether **16** with retention of the keto group and configurations of all assymmetric centres. This is the first example of the successful vinylation of a hydroxy ketone.[41,92]



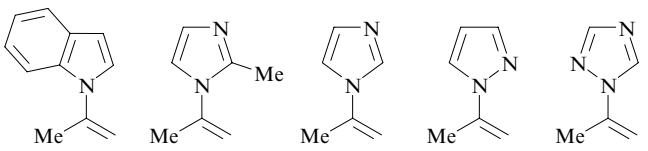
R = C_8H_{17} (**13**, **14**), Ac (**15**, **16**).

In the presence of the system KOH – DMSO, pyrroles were vinylated for the first time under relatively mild conditions with a methylacetylene – allene mixture to produce *N*-isopropenylpyrroles **17** in good yields.[93]



R^1 = R^2 = H, Me; R^1 – R^2 = $(CH_2)_4$.

This catalyst can also be used in the isopropenylation of other azoles (105 – 145 °C, 5 – 15 h), namely, indoles, imidazoles, pyrazoles, triazoles. The corresponding *N*-isopropenyl derivatives **18** – **22** were obtained in yields of 20% – 70% (non-optimised yields).[94]

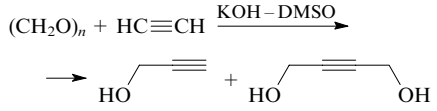


The above (hardly exhaustive) examples illustrate the impressive advances in the studies of vinylation with acetylenes, which were observed in the past decades due to the use of superbasic catalytic systems.[7,41]

c. The Favorsky alkynol synthesis and its analogues

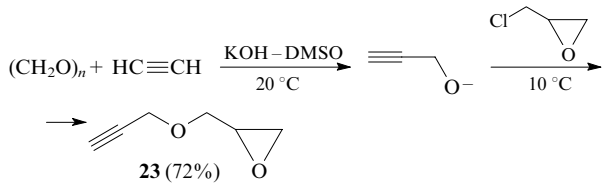
The quantum-chemical analysis[95–97] shows that in the gas phase or a weakly solvating medium the formation of acetylide anions from acetylene under the action of superbases at low temperatures is more preferential than the alternative nucleophilic addition of anions to the triple bond. Hence, superbases should accelerate the Favorsky ethynylation of aldehydes and ketones (the addition of acetylide anions to the C=O bond).

Indeed, it was shown that in the superbasic medium KOH–DMSO, acetylene reacts quickly and quantitatively with paraform at the atmospheric pressure and room temperature to form propargyl alcohol[98–100] and/or but-2-yne-1,4-diol.[33,41] In contrast to the classical vinylation of formaldehyde, which proceeds in the presence of an explosive copper acetylide under a pressure of up to 70 atm and at a temperature of 90–130 °C, the new method allows one to make, if required, propargyl alcohol the main reaction product (yield up to 90%).[99]

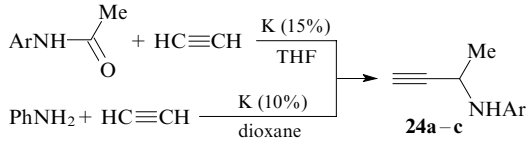


Other aldehydes and ketones also react with acetylene more actively in the presence of the system KOH–DMSO than under conventional conditions; moreover, different acetylenic alcohols and glycols can be synthesised in high yields with no recourse to high pressures, cooling and large volumes of solvents,[7,33,101] *i.e.*, in the absence of all attributes inherent in the classical ethynylation.

In the system KOH–DMSO, the one-pot synthesis of glycidyl propargyl ether (**23**) was carried out from paraform, acetylene and epichlorohydrin.[102]

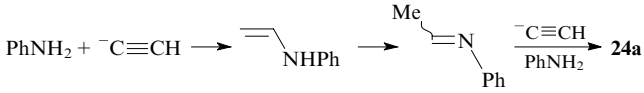


Acetylide anions generated from acetylene in superbasic media add to the C=N bond. Thus anilides[103–105] and anilines[106] react with acetylene in the presence of their potassium derivatives (at 160 °C, under enhanced pressure, in THF or dioxane) to form 3-arylaminobutynes **24a–c**.



Ar = Ph (**a**), 2-MeC$_6$H$_4$ (**b**), 4-MeC$_6$H$_4$ (**c**).

It was proved that these reactions proceed through the intermediate formation of the Schiff base that adds the acetylide anion to the C=N bond (the aza analogue of the Favorsky reaction).[103,105]

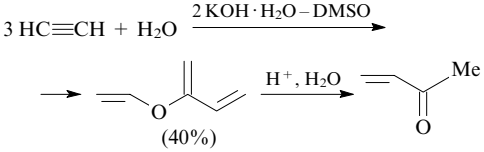


2. New reactions

Several new general reactions of acetylene that occur in superbasic media and produce promising monomers and synthons for the fine organic synthesis have been discovered.[7,28–36,40–43]

a. Hydrative trimerisation of acetylene

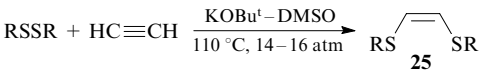
It was found that in the presence of the complex 2 KOH·H$_2$O–DMSO (80–115 °C, 10–15 atm), three acetylene molecules and one water molecule undergo a single-stage formation of 2-vinyloxybuta-1,3-diene that simultaneously contains a 1,3-diene fragment and a vinyl group.[107,108]



Mild acid-catalysed hydrolysis of 2-vinyloxybuta-1,3-diene (1% HCl, 20 °C) affords methyl vinyl ketone in the quantitative yield.[33]

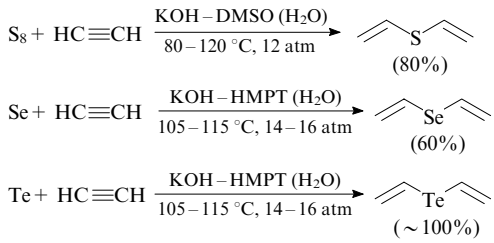
b. Direct vinylation of chalcogens and elemental phorphorus

The use of superbasic systems made it possible to carry out a series of unconventional acetylene reactions, particularly, the direct vinylation of chalcogens and elemental phosphorus in the presence of a minimum amount of a proton donor (usually, water). These studies were initiated by the discovery of a reaction of acetylene incorporation into the S–S bond of disulfides in the system KOBu^t–DMSO. The reaction is stereoselective and produces *Z*-isomers of 1,2-bis(alkylthio)-ethenes **25**.[109–111]



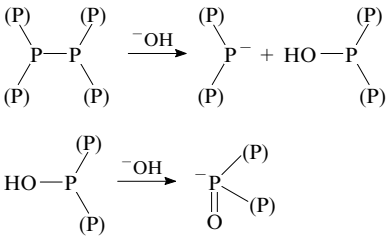
R = Me, Et, Bu^n, Bu^i.

As was found later, this reaction is general and may be extended to dialkyl diselenides[112] and elemental S_8, Se and Te.[111,113–115] Being a supernucleophile, the polysulfide anion formed from the cyclic octamer S_8 is easily captured by acetylene. As a result of subsequent transformations, the polysulfide anion transforms into divinyl sulfide in the presence of proton donors.[111,113,114] Selenium and tellurium are vinylated to divinyl selenide and divinyl telluride, respectively, in the presence of the system KOH–HMPT (HMPT is hexamethylphosphotriamide).[111,114,115] In this reaction, superbases act not only as the catalysts but also as the reagents, being involved in the redox disproportionation of selenium or tellurium.

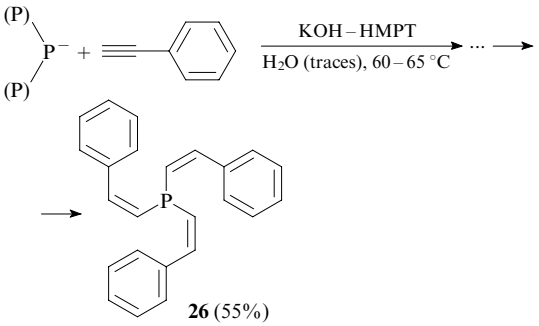


Under these conditions, elemental phosphorus behaves in a similar way. Under the action of an activated hydroxide

ion, the P—P bonds of both white and red phosphorus are easily cleaved to form phosphide and phosphinite anions,† which react with the appropriate electrophile (complementary with respect to symmetry and population of unoccupied valence molecular orbitals).[35, 116–120]

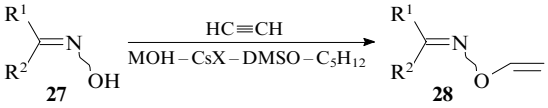


For phosphide anions, acetylenes proved to be these complementary electrophiles. Thus the reaction of phosphide anion with phenylacetylene at 60–65 °C proceeds by a stereoselective mechanism to form a *Z*,*Z*,*Z*-isomer of tristyrylphosphine (**26**).[35, 117–119]



c. Synthesis of *O*-vinylketoximes

Nucleophilic addition of ketoximes **27** to acetylene in superbasic media to form *O*-vinylketoximes **28** made the latter easily accessible.[42, 121–124]

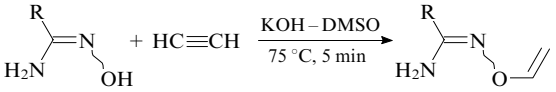


R^1, R^2 = Alk, Ar, Het; M = Li, Na, K; X = Cl, F.

The highest yield of vinyloximes **28** was reached due to the modification of the superbasic system MOH–DMSO by the addition of a non-polar solvent (pentane) and caesium halides. Pentane extracts the *O*-vinyloximes formed and thus prevents their further transformation to pyrroles, while caesium salts are converted to CsOH due to the exchange processes thus providing the high basicity of the system.[121–123]

d. Synthesis of *O*-vinylamidoximes

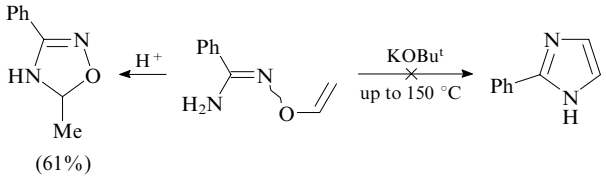
The use of superbasic catalysts made it possible to vinylate amidoximes, which are prone to tautomeric transformations under ordinary conditions.[125, 126]



R = Me (46%), Ph (89%).

† In the first stages, phosphide and phosphinite anions represent supernucleophilic anionic clusters.

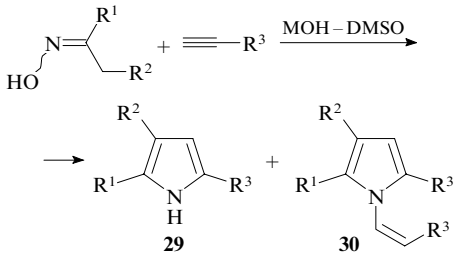
Chemoselective vinylation at the hydroxyl group occurs at a temperature unusually low for this reaction (75 °C) very quickly, virtually instantaneously (it takes about 5 min for the reaction to be completed).[125, 126] The resulting *O*-vinylamidoximes form a new class of promising monomers and synthons, particularly, for designing heterocycles. For example, they are easily cyclised to oxodiazolines,[41] although the attempts to rearrange them into imidazoles (analogously to the rearrangement of *O*-vinyloximes to pyrroles[42, 127]) failed so far.



e. Acetylene reactions with ketoximes: synthesis of pyrroles

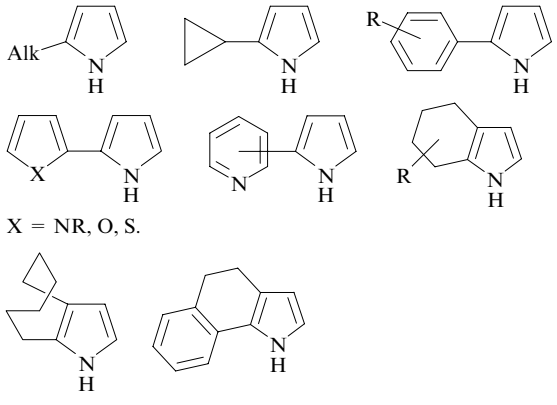
A new general reaction of ketoximes with acetylenes, which proceeds in superbasic media such as MOH–DMSO (M is an alkali metal) and afford pyrroles **29** and *N*-vinylpyrroles **30**, was discovered.[30, 32–34, 37, 41, 42 127–144] An excess of acetylene favours direct formation of *N*-vinylpyrroles **30**. Actually, this reaction represents a two-stage transition from ketones to diverse pyrroles.

By this reaction, virtually any ketone that has at least one methylene or methyl group in the α-position with respect to the carbonyl function and contains no strong base-sensitive substituents can be transformed into the corresponding pyrrole or *N*-vinylpyrrole. If necessary, a one-pot synthesis can be carried out in the system MOH–DMSO. For this purpose, a ketone is treated first with hydroxylamine (or its hydrochloride) and then with acetylene.[143]



R^1, R^2 = Alk, Ar, Het; R^3 = H, Me, Ph; M = Li, Na, K, Rb, Cs.

This reaction has provided a facile route to pyrroles with alkyl, cycloalkyl, aryl and hetaryl substituents and pyrroles annulated with common rings, macrocycles and fused systems.[7, 30, 41, 140–146]

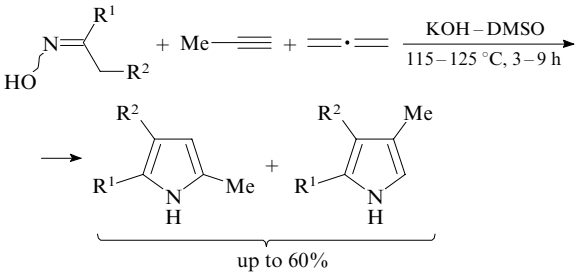


X = NR, O, S.

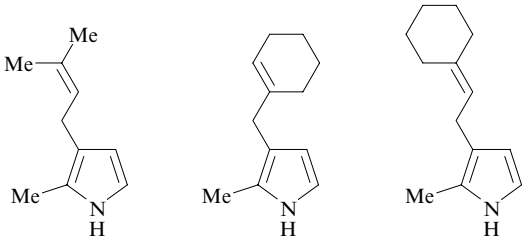
At present, this reaction is widely referred to in the literature as the Trofimov reaction (*e.g.*, see Refs 147–157).

Alkali metal hydroxides were used as the MOH component of the superbasic catalytic system MOH–DMSO. Rubidium and caesium hydroxides are more active than KOH but the latter is much cheaper; this is why the system KOH–DMSO is used, as a rule. Lithium and sodium hydroxides are less active; however, they allow one to obtain NH pyrroles more selectively, because they virtually do not catalyse their vinylation. In the absence of DMSO, pyrroles are not formed, *i.e.*, the intrinsic basicity of alkali metal hydroxides is insufficient and this reaction requires superbasicity.[41]

In place of acetylene, methylacetylene and allene can be employed.[93]

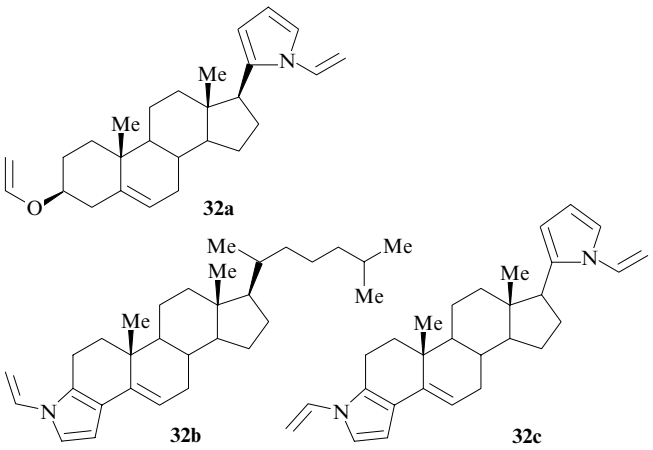


This reaction was successfully used for the synthesis of pyrroles **31a–c** with terpenoid substituents.[7,41,131] For this purpose, terpenoid ketones were treated first with hydroxylamine and then with acetylene in the system KOH–DMSO.



31a (80%) **31b** (60%) **31c** (40%)

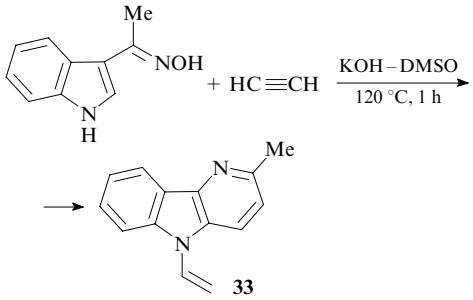
This reaction was also used to prepare recently unknown steroid pyrrole compounds including those containing highly reactive *O*- (compound **32a**) and *N*-vinyl (**32a–c**) groups capable of polymerisation and further chemical modification.[41,134,136,137]



32a **32b** **32c**

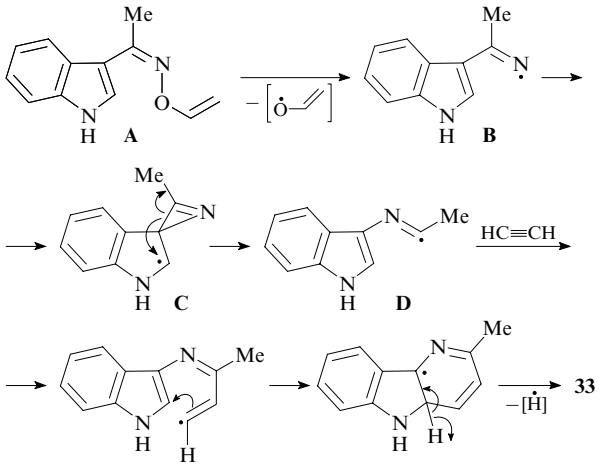
f. Synthesis of δ-carboline from 3-acetylindole oxime and acetylene

The reaction 3-acetylindole oxime with acetylene in the superbasic catalytic system KOH–DMSO opened up a new way (one-pot assembling) to the synthesis of δ-carboline system, namely, pyridoindole **33**, which was difficult to synthesise earlier.[158]



33

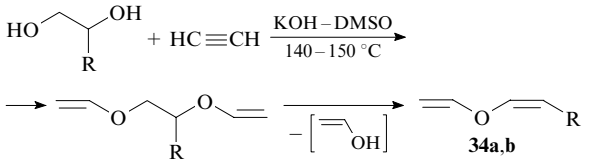
Apparently, this reaction proceeds through the homolytic cleavage of the N–O bond in the intermediate *O*-vinyloxime **A** followed by the intramolecular attack of iminyl radical **B** on the pirrole ring. After this, the homolytic opening of the spiroazirine intermediate **C** and the addition of the second acetylene molecule to radical **D** complete closure of the pyridine ring.[158]



Carboline structures are present in many natural compounds and medicinal drugs; however, so far the synthesis of δ-carbolines remained an unsolved problem in the chemistry of indole alkaloids. An important advantage of this reaction is the possibility of the one-stage synthesis of the hitherto unknown *N*-vinyl-δ-carbolines.[42] The latter combine the properties of an *NH*-protected δ-carboline with those of highly reactive synthons and monomers, which opens up wide prospects for the development of the fundamental and synthetic chemistry of indole alkaloids and high-molecular-weight compounds of the carboline series.

g. Eliminative vinylation of 1,2-diols and polyols

The eliminative vinylation of 1,2-diols and polyols opened up a rational way to divinyl ethers, namely, vinyloxyalkenes **34**.[33] The formal elimination of vinyl alcohol from the intermediate divinyl ethers proceeds only in the presence of superbases such as KOH–DMSO; moreover, the elimination proceeds more smoothly in the presence of acetylene.[159,160]



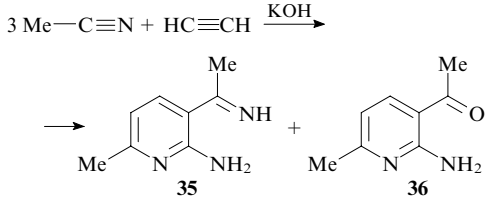
34a,b

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

Due to this reaction, divinyl ethers, the promising monomers and synthons, have become accessible for the first time and the reaction itself, being general, has supplemented the arsenal of methods of organic chemistry.[33]

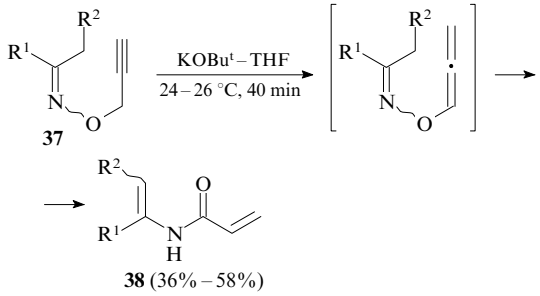
h. Cyclo-co-oligomerisation of acetylene with acetonitrile

The cyclisation of acetylene with three acetonitrile molecules pertains to the new reactions of acetylene that proceed in superbasic media. The cyclisation occurs under mild conditions (from −10 to 20 °C, atmospheric pressure, a superbasic system KOH – MeCN) and leads to 2-amino-3-(2-iminoethyl)-6-methylpyridine (**35**), the first representative of pyridines that simultaneously contains an imine and an amine functions, and 3-acetyl-2-amino-6-methylpyridine (**36**).[161]



i. Rearrangement of *O*-propargylketoximes

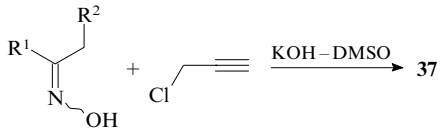
In the presence of a specific superbasic system KOBu^t – THF, propargyl ethers of ketoximes **37** are rearranged to *N*-vinylacrylamides **38** rather than to the expected allenyl ethers (room temperature, exothemic process). This rearrangement is general.[162]



38 (36% – 58%)

R^1 = Alk, Ar; R^2 = H, Alk.

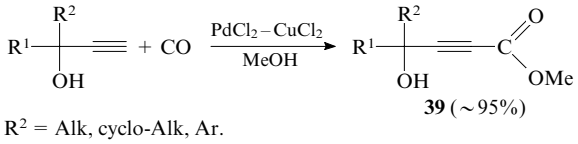
In turn, *O*-propargylketoximes **37** are obtained in quantitative yields from oximes and propargyl chloride in the superbasic system KOH – DMSO.[41,163] It is amazing that this virtually universal catalytic system fails to induce the rearrangement of *O*-propargylketoximes formed.



III. Chemistry of acetylenic hydroxy acids and their derivatives

1. Oxidative methoxycarbonylation of acetylenic alcohols

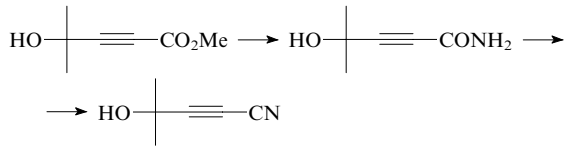
The direct catalytic synthesis of methyl esters of acetylenic hydroxy acids **39** was carried out by the reaction of acetylenic alcohols with carbon monoxide in methanol in the presence of palladium and copper chlorides.[31,33] In contrast to the classical Reppe carbonylation, which affords the acrylic systems, in this case, the triple bond remains intact. The presence of an acceptor group near the triple bond in compounds **39** dramatically enhances the reactivity of this bond, which makes these compounds the promising reagents for the fine organic synthesis.



39 (~95%)

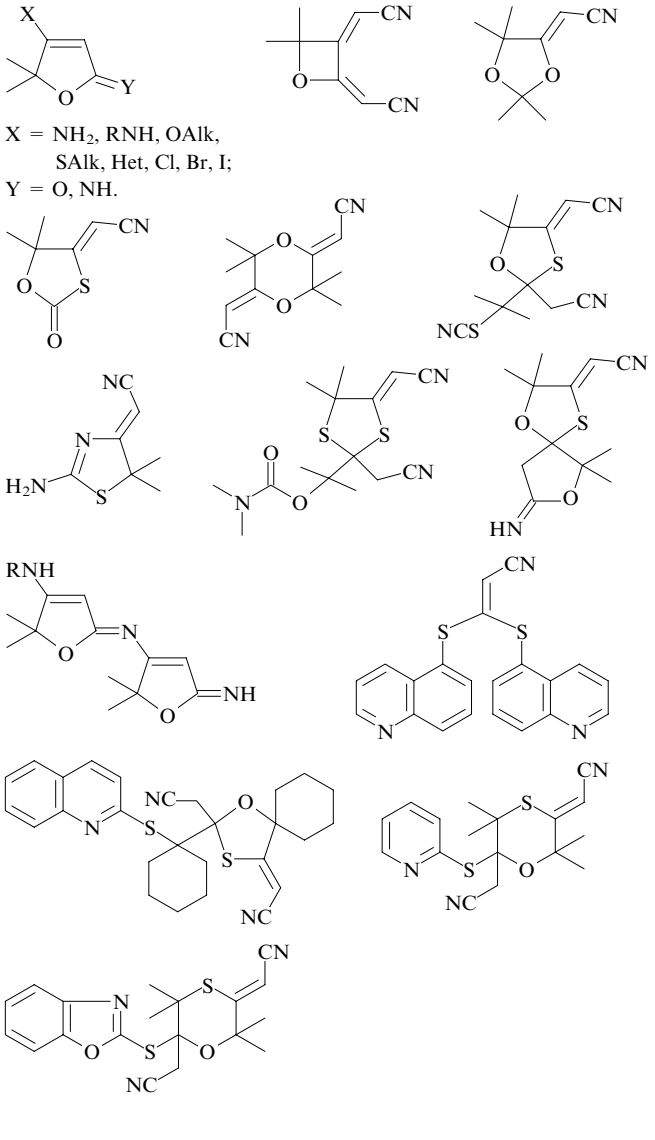
R^1, R^2 = Alk, cyclo-Alk, Ar.

The reaction of oxidative methoxycarbonylation of acetylenic alcohols provided reliable synthetic grounds to the chemistry of acetylenic hydroxy acids and their derivatives.[31,38]



2. Addition of nucleophiles

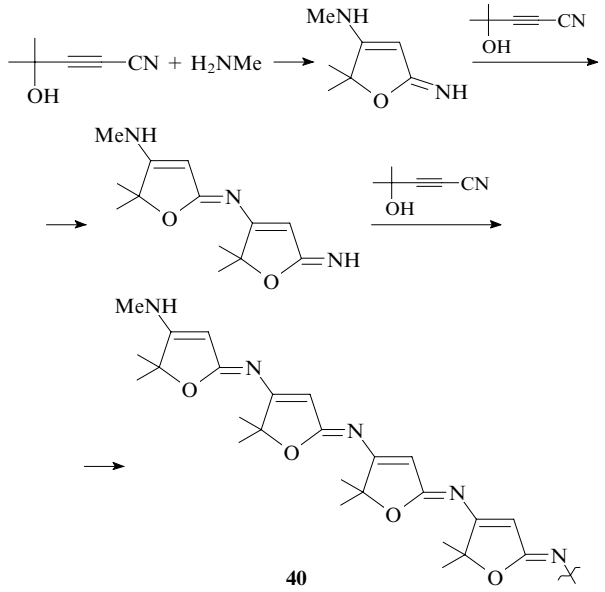
The addition of different nucleophiles (alcohols, thiols, amines, cyanide anion) to esters and nitriles of α,β-acetylenic γ-hydroxy acids followed by the cyclisation under biomimetic conditions (room temperature, aqueous medium) opened up new approaches to the synthesis of functionalised heterocycles, which were difficult to prepare. Below, the examples of compounds synthesised by this approach are shown.[7,31,38,164–172]



X = NH_2, RNH, OAlk, SAlk, Het, Cl, Br, I;
Y = O, NH.

This strategy can be applied to the directed synthesis of biologically important derivatives of tetronic, ascorbic and penicillic acids and other antibiotics of this series, particularly, the promising anti-HIV drugs.[38]

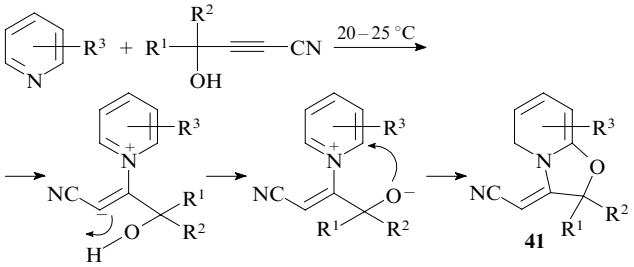
The nucleophilic addition of amines to nitriles of hydroxy acetylenic acids affords conjugated poly(iminodihydrofurans) **40** with unusual electrophysical properties.[173–178]



40

3. Synthesis of fused pyridine systems

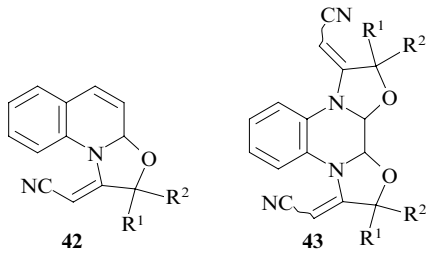
An unexpected regiospecific cyclisation of nitriles of hydroxy acetylenic acids with pyridine and its methyl derivatives (α-, β- and γ-picolines), which occurs at room temperature in the absence of catalysts and solvents, leads to the formation of (*Z*)-cyanomethylidene-1,3-oxazolidino[3,2-*a*]-1,2-dihydropyridines **41** in high yield. The latter compounds serve as the reactive building blocks in the fine organic synthesis, the promising biologically active compounds and polydentate ligands for the design of metal-complex catalysts.[179]



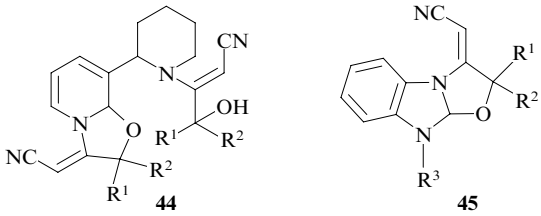
41

$R^1 = R^2 = Me$, $R^1 - R^2 = (CH_2)_5$; R^3 = H, 2-Me, 3-Me, 4-Me.

Later, this reaction was extended to the functional pyridine derivatives[180–184] and 1-substituted benzimidazoles.[185] Hence, this is a general reaction. It was used for the syntheses of oxazolidinoqinolines **42**,[181] bis(oxazolidino)quinoxalines



42 **43**



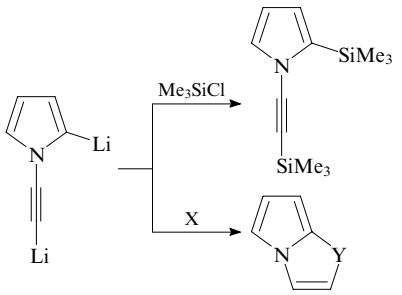
44 **45**

43,[181] substituted (oxazolidinopyridinyl)piperidines **44**,[183] oxazolidinobenzimidazoles **45**.[185]

IV. Acetylene- and allene-derived carbanions

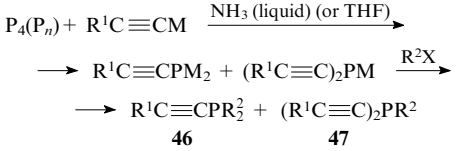
In the past decade, a considerable contribution was made to the chemistry of carbanions of the acetylene and allene seties.[186–192]

The functionalisation of the pyrroloacetylene dianion with trimethylchlorosilane and chalcogens afforded 2-trimethylsilyl-1-trimethylsilylethynylpyrrole, pyrrolo[2,1-*b*]thiazole and the hitherto unknown fused heterocyclic systems, namely, pyrrolo[2,1-*b*]selenazole and pyrrolo[2,1-*b*]tellurazole.[186]



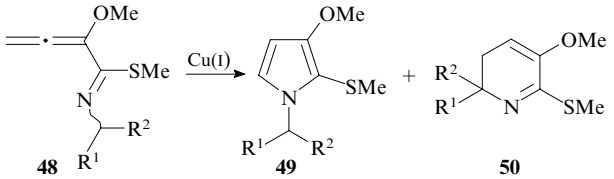
X = S_8, Se, Te; Y = S, Se, Te.

A direct reaction of elemental phosphorus with the acetylenide ions generated from acetylenes under the action of a strong base served as the basis of a new convenient approach to the formation of the $C_{sp}-P$ bond and the synthesis of acetylenic phosphines **46** and **47**, the promising monomers, reagents, intermediates and ligands for the production of effective metal-complex catalysts, which were difficult to synthesise.[187, 188, 190]



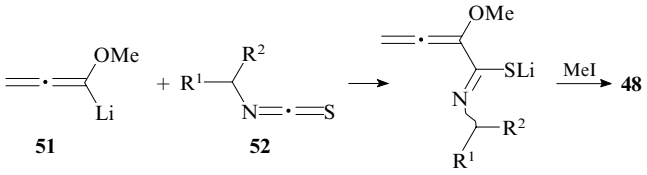
R^1 = Alk, Ph; R^2 = Alk; M = Li, Na; X = Br, Cl.

A new direction in the organic and organometallic chemistry has been developed. This concerns the low-temperature reactions of carbanions derived from alkynes and allenes with isothiocyanates.[7, 189, 191, 192] Based on these reactions, new convenient approaches to the synthesis of fundamental heterocyclic systems, namely, derivatives of pyrrole, pyridine, quinoline and thiophene, were developed.[189, 191–204] Thus the copper salt-catalysed cyclisation of azatrienes **48** produced 1-alkyl-3-methoxy-2-methylthiopyrroles **49** and their isomers, 2,3-dihydropyridines **50** in the total yield of 80%.



48 **49** **50**

Azatrienes **48** are easily formed from 1-lithio-1-methoxyallene (**51**) and alkyl thiocyanates **52**.[189, 191–193, 203]



51 **52** **48**

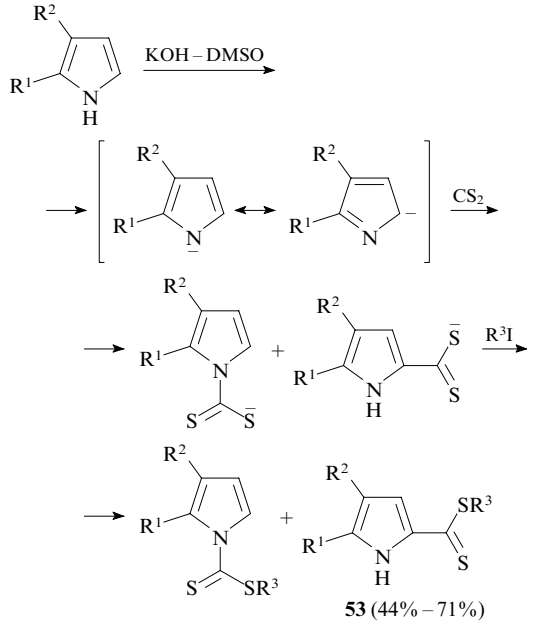
R^1, R^2 = Alk.

V. New reactions involving pyrrole

The systematic elaboration of acetylene reactions with ketoximes (the Trofimov reaction) made accessible a virtually unlimited series of substituted pyrroles, which served as a new impetus for further development of the chemistry of pyrrole compounds.[7, 30, 32–34, 37, 39–46, 129, 205–208] Although the discussion of pyrroles is beyond the frames of this review, we, nonetheless, decided to discuss several new reactions involving these compounds.

1. Ambident pyrrole anions in the synthesis of alkyl pyrrole-2-dithiocarboxylates

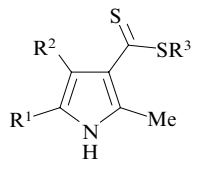
A method was developed for the synthesis of alkyl pyrrole-2-dithiocarboxylates **53** by the pyrrole reaction with carbon disulfide and alkyl halides at room temperature in the superbasic system KOH–DMSO.[209–211]



53 (44%–71%)

R^1 = Me, Ph; R^2 = H, Me; R^1–R^2 = $(CH_2)_4$;
R^3 = Et, Bu, CH_2=$CHCH_2$.

In the presence of substituents in both α-positions of the pyrrole ring, pyrrole-3-carbodithioates **54a–g** are exclusively formed in yields of 36%–61%.[212]

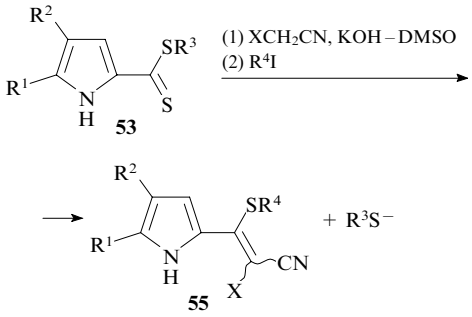


54a–g

Compound	R^1	R^2	R^3
54a	Me	H	Et
54b	Me	Me	Et
54c	$(CH_2)_4$		Et
54d	$(CH_2)_4$		Bu
54e	Ph	H	Et
54f	2-furyl	H	Et
54g	2-thienyl	H	Et

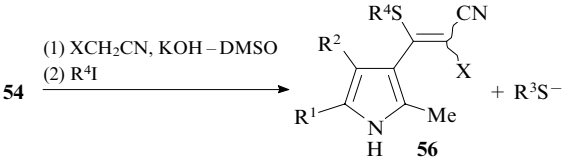
2. Synthesis of functional 2- and 3-vinylpyrroles

A simple, general and reliable approach to the synthesis of 2-(**55**) and 3-(1-alkylthio-2-cyanovinyl)pyrroles (**56**) has been found, which is based on the reaction of pyrrole-2- (**53**) and pyrrole-3-carbodithioates (**54**) with nitriles containing an active methylene function (with malononitrile and cyanoacetamide) followed by alkylation of the intermediate thiolate.[39, 40, 213–216]



53 **55**

R^1 = Me, Ph; R^2 = H, Me; R^1–R^2 = $(CH_2)_4$;
R^3, R^4 = Alk; X = CN, $CONH_2$.

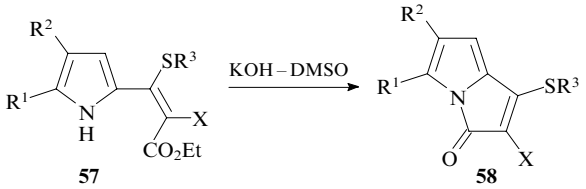


54 **56**

R^1 = Me, Ph, 2-furyl, 2-thienyl; R^2 = H, Me;
R^1–R^2 = $(CH_2)_4$; R^3, R^4 = Alk; X = CN, $CONH_2$.

3. Cyclisation of functionally substituted 2-vinylpyrroles to 3*H*-pyrrolizin-3-ones and 3*H*-iminopyrrolizines

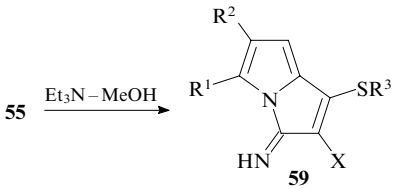
On heating (55–100 °C) in the system KOH–DMSO, the functionally substituted 2-vinylpyrroles **57** undergo intramolecular cyclisation to form earlier unknown 3*H*-pyrrolizin-3-ones **58**.[217, 218]



57 **58**

R^1 = Ph, R^2 = H; R^1–R^2 = $(CH_2)_4$; R^3 = Alk;
X = CN, COMe, CO_2Et.

By the example of 2-[(alkylthio)cyanovinyl]pyrroles **55**, it was shown that cyclisation in the system Et_3N–MeOH leads to 3*H*-iminopyrrolizines **59**.[218, 219]



59

R^1 = Ph, R^2 = H; R^1–R^2 = $(CH_2)_4$; R^3 = Alk; X = CN, $CONH_2$.

4. Nucleophilic substitution of an amino group for the alkylthio group in 3*H*-pyrrolizin-3-ones

Under mild conditions (20–25 °C, 15 min), 3*H*-pyrrolizin-3-ones **58** react quickly and quantitatively with secondary amines to form aminopyrrolizin-3-ones.[218]



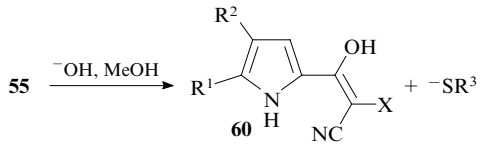
58

R^1 = Ph, R^2 = H; R^1-R^2 = $(CH_2)_4$; R^3-R^5 = Alk;
X = CN, $CONH_2$, CO_2Et.

A similar exchange was observed for 3-imino-4,5,6,7-tetrahydrocyclohexa[*c*]-3*H*-pyrrolizines.[219–222]

5. Enols of the pyrrole series

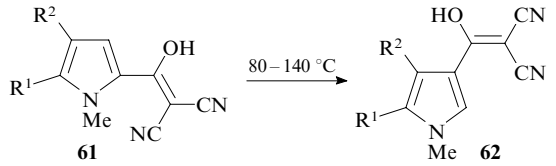
On treatment with NaOH, the alkylthio group in 2-[(alkylthio)cyanovinyl]pyrroles **55** is easily (40–45 °C, 1 h) displaced by a hydroxyde ion to form stable enols, namely, 2-(1-hydroxy-2-cyanovinyl)pyrroles **60** in the yield of up to 90%.[223]



R^1 = Me, Ph; R^2 = H, Me; R^1-R^2 = $(CH_2)_4$; R^3 = Alk;
X = CN, $CONH_2$.

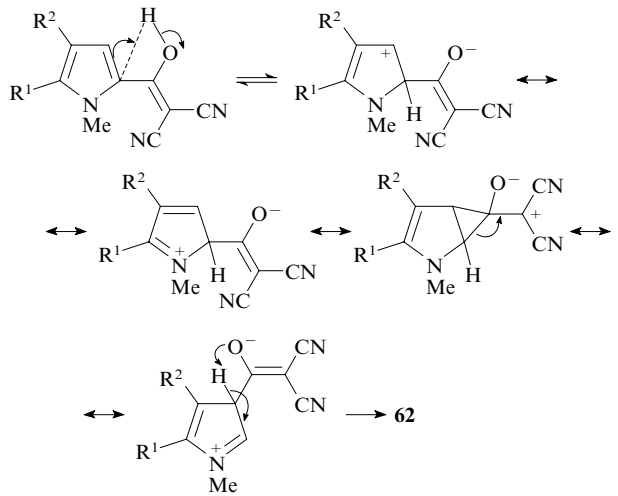
This reaction opened up a new way to the new class of stable enols with pyrrole substituents, which are the promising subjects for studying the fundamental problems of reactivity, the theory of chemical bonds, the electron transfer in conjugated systems, the hydrogen bond and tautomerism. The synthesised enols are also highly reactive building blocks for targeted synthesis of new medicinal drugs and materials.

On heating, enols **61** are rearranged into 3-isomers **62**. This is the first example of the migration of a functional substituent from the α- to β-position in the pyrrole ring.[224]



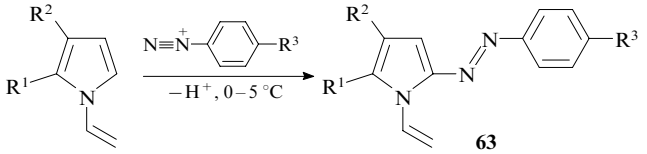
R^1 = R^2 = H; R^1-R^2 = $(CH_2)_4$.

Obviously, the easy migration of the enol fragment is due to the enhanced acidity of the hydroxyl function (the effect of two strong electron-withdrawing CN groups in the conjugated system) and the sensitivity of the pyrrole ring with respect to protonation.[224]



6. 2-Arylazo-1-vinylpyrroles

To extend the synthetic potential of 1-vinylpyrroles and assess the relative reactivity of the vinyl group and the pyrrole ring with respect to different cations, the reaction of 1-vinylpyrroles with aryldiazonium salts was studied. The use of this reaction made possible a highly efficient synthesis of 2-arylazo-1-vinylpyrroles **63**,[225,226] which are promising compounds for the development of electrochromic devices, optical switches and materials for non-linear optics.



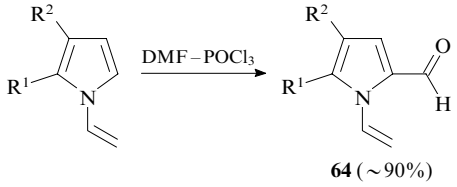
63

R^1 = H: R^2 = H, Me, Ph, 4-$MeOC_6H_4$, 2-furyl, 2-thienyl;
R^1-R^2 = $(CH_2)_4$; R^3 = H, Br, Me, OEt, NO_2, 4-$N_2C_6H_4$.

Based on 2-arylazo-1-vinylpyrroles, coloured polymers were synthesised as well as palladium complexes, which are promising catalysts of cross-coupling reactions.[225]

7. 1-Vinylpyrrole-2-carbaldehydes

The efficient formylation of *N*-vinylpyrroles was carried out under mild conditions (0–20 °C) according to the modified Vilsmeier–Haack reaction to produce a new, previously unknown class of functional pyrroles, namely, 1-vinylpyrrole-2-carbaldehydes **64**.[227]



64 (~90%)

R^2 = H: R^1 = Me, Ph; R^1-R^2 = $(CH_2)_4$.

The simultaneous presence of two reactive groups (vinyl and aldehyde) in vinylpyrrolecarbaldehydes **64** makes them promising reagents for the fine organic synthesis.[228]

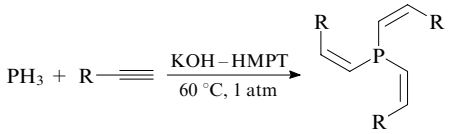
VI. The use of acetylenes in the synthesis of phosphines and phosphine chalcogenides

A new approach to the formation of the C–P bond, which was discovered by the example of the reaction of phenylacetylene with elemental phosphorus, has been systematically developed.[35,116–119,229] This approach is based on the use of phosphorus-centred anions generated from elemental phosphorus in heterogeneous superbasic media such as KOH–DMSO or KOH–H_2O–organic solvent–phase-transfer catalyst. These studies allowed the commercially manufactured electrophiles to be directly phosphorylated with elemental phosphorus (or with a phosphine generated from phosphorus) and also the highly efficient syntheses of phosphines and phosphine chalcogenides.[230–240] The thus obtained primary and secondary phosphines and phosphine chalcogenides are the promising PH-addends for the addition to multiple bonds.

1. Nucleophilic addition of primary and secondary phosphines to acetylenes

Superbases proved to be good catalysts for the vinylation of phosphines under the action of aryl- and hetarylacetylenes.

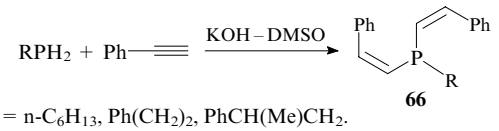
At 60 °C and atmospheric pressure, the reaction is stereoselective to afford *Z*,*Z*,*Z*-isomers of tristyrylphosphine (**26**) and its analogues **65a–d** in the yields of up to 80%.[36, 117, 119, 240–243]



26, **65a–d**

R = Ph (**26**), 4-FC_6H_4 (**65a**), 2-Py (**65b**), 2-furyl (**65c**), 2-thienyl (**65d**).

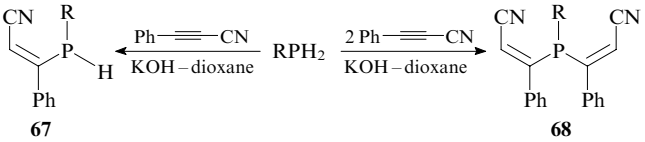
Primary alkyl- and arylphosphines add to phenylacetylene in the system KOH–DMSO (60 °C, 1–4 h) to form *Z*,*Z*-isomers of distyrylphosphines **66**.[244]



66

R = n-C_6H_{13}, $Ph(CH_2)_2$, $PhCH(Me)CH_2$.

An activated alkyne [cyano(phenyl)acetylene] reacts with alkylphosphines under mild conditions (KOH–dioxane, 20–22 °C) to form either secondary (compound **67**) or tertiary (compounds **68**) phosphines in the *Z*-configuration (yield 70%–91%) depending on the rectant ratio.[245]

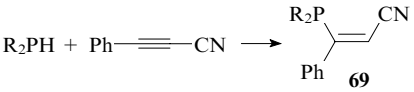


67 **68**

R = Alk.

It was experimentally proved (based on the EPR and UV spectroscopic data) that the reaction proceeds through a single-electron transfer.[245]

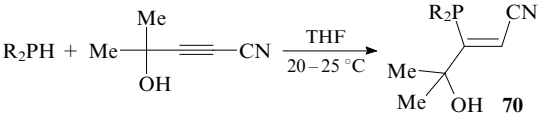
Secondary phosphines readily react with cyano(phenyl)acetylene in the absence of catalysts to form monoadducts **69** preferentially in the *Z*-configuration.[246] According to the results of EPR and UV spectroscopic studies, this reaction also involves the single-electron transfer stage.[246]



69

R = $Ph(CH_2)_2$, $PhCH(Me)CH_2$.

Based on the reaction of secondary phophines with 4-hydroxy-4-methylpent-2-ynonitrile, a convenient, efficient and stereo-controlled method for the synthesis of functionally substituted tertiary phosphines **70** containing hydroxyl and nitrile groups has been developed.[245, 247]

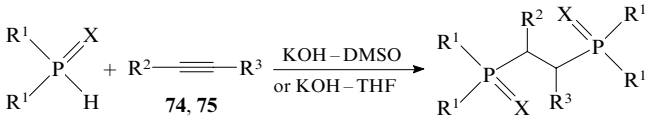


70

R = Bu, $Ph(CH_2)_2$, 2-$Py(CH_2)_2$.

2. Nucleophilic addition of primary and secondary phosphine chalcogenides to acetylenes

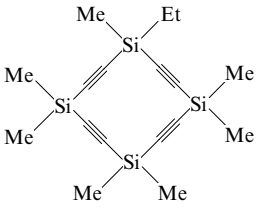
Secondary phosphine oxides **71** [X = O, R^1 = $Ph(CH_2)_2$], **72** (X = O, R^1 = Ph) and phosphine sulfides **73** [X = S, R^1 = $Ph(CH_2)_2$] react virtually quantitatively with methylacetylene (**74**) (R^2 = H, R^3 = Me)[248] and cyano(phenyl)acetylene (**75**) (R^2 = Ph, R^3 = CN)[249] in the presence of superbases KOH–DMSO (Ref. 248) or KOH–THF (Ref. 249) to form phosphine oxides **76**, **77** and phosphine sulfide **78** containing chiral carbon centres.



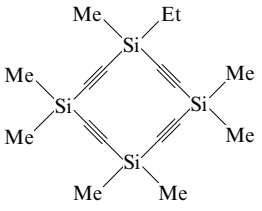
71–73 **74, 75** **76–78**

Compound	X	R^1	R^2	R^3
76	O	$Ph(CH_2)_2$	H	Me
77	O	Ph	Ph	CN
78	S	$Ph(CH_2)_2$	Ph	CN

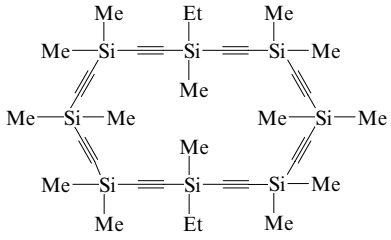
Compounds **76–78** are the promising intermediates for the synthesis of optically active phosphine ligands, which are widely used in the catalytic stereospecific synthesis.



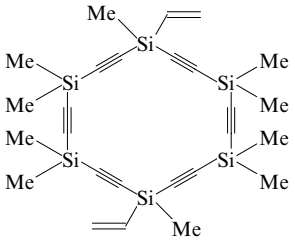
79



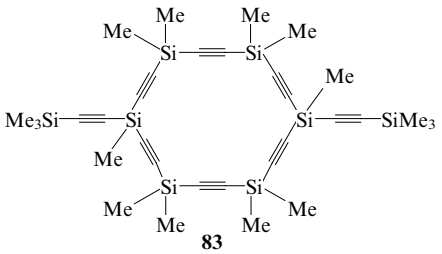
80



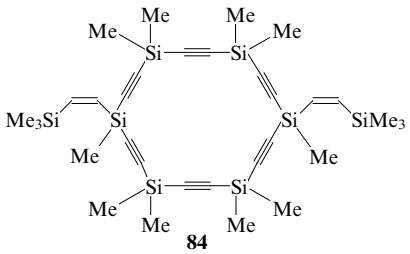
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82



83



84

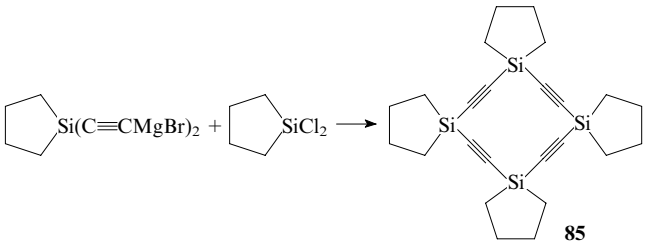
VII. Acetylene derivatives of silicon and germanium

M G Voronkov and co-workers have developed the synthetic approaches to macrocyclic silaalkynes [250–273] and silicon-and-chalcogen-containing heterocyclic compounds.[274–277]

1. Synthesis of acetylene- and silicon-containing macrocycles

Based on the condensation reaction of the bromomagnesio derivatives of dimethyldiethynyl- and methyl(vinyl)diethynylsilane, bis(dimethylethynylsilyl)ethyne, dimethylbis(dimethylethynylsilylethynyl)silane, *etc.* with dialkyl-, ethyl(methyl)-, methyl(trimethylsilylethynyl)- and methyl(2-trimethylsilylvinyl)dichlorosilanes, a general method of synthesis of methylorganylcyclosilaalkynes **79–84** $(MeRSiC{\equiv}C)_n$ ($n = 4–8$) containing exocyclic substituents (R = H, Me, Et, $CH_2{=}CH$, $Me_3SiC{\equiv}C$, $Me_3SiCH{=}CH$) was developed.[257–259, 261, 263]

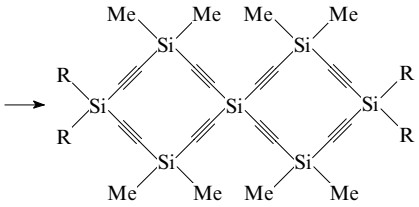
12-Membered cyclosilaethyne **85** of the propellane type was synthesised by the reaction of 1,1-bis(bromomagnesioethynyl)silacyclopentane with 1,1-dichlorosilacyclopentane.[265]



85

Spiromacrocyclic polysilaalkynes **86** and **87** were synthesised by the condensation of bromomagnesio derivatives of dialkylbis(dimethylethynylsilylethynyl)silane with silicon tetrachloride.[264]

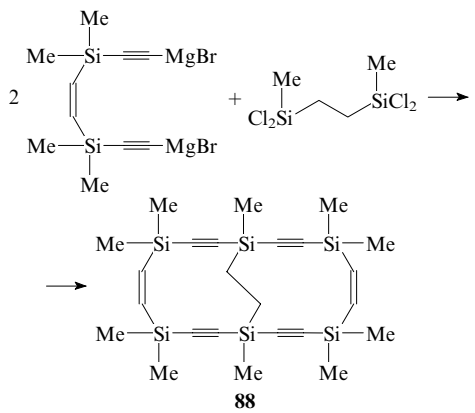
$$2\ R_2Si(C{\equiv}CSiMe_2C{\equiv}CMgBr)_2 + SiCl_4 \longrightarrow$$



86, **87**

R = Me (**86**), Et (**87**).

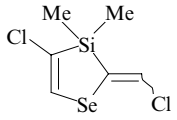
The (*E*)-1,2-bis(bromomagnesioethynyldimethylsilyl)-ethene reaction with 1,2-bis(methyldichlorosilyl)ethane produced an unusual macrobiocyclic compound **88**, which contained both unsaturated and saturated endocyclic groups ($SiC{\equiv}CSi$, $SiCH{=}CHSi$, $SiCH_2CH_2Si$).[270]



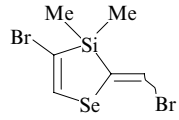
88

2. New five-membered silicon-and-chalcogen-containing heterocycles

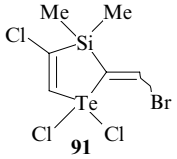
New unsaturated heterocycles of the fulvene (compounds **89–91**) or cyclopentene (compound **92**) types, which contain silicon, selenium and tellurium atoms, were synthesised from dimethyldiethynylsilane and selenium and tellurium tetrahalides under mild conditions (20–25 °C, $CHCl_3$) in good or moderate yields.[274–277]



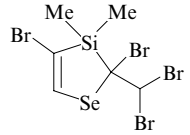
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90



91

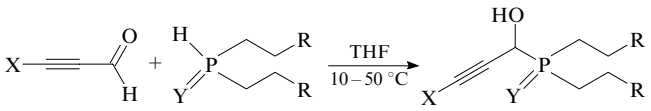


92

3. Silicon- and germanium-containing acetylene aldehydes

The reactivity of 3-(trimethylsilyl)- (**93**, X = Me_3Si) and 3-(triethylgermyl)prop-2-ynals (**94**, X = Et_3Ge), which are easily prepared by the oxidation of the corresponding 3-trimethylsilyl- and 3-(triethylgermyl)prop-2-ynols [278–285] with the activated system $MnO_2–SiO_2$ [286] or pyridinium chlorochromate [287] under microwave radiation in the absence of a solvent, was studied. Being ambident 1,3-biselectrophiles, propynals **93** and **94** react with nucleophiles chemoselectively involving the triple bond, the carbonyl group or both reaction centres.[288–298]

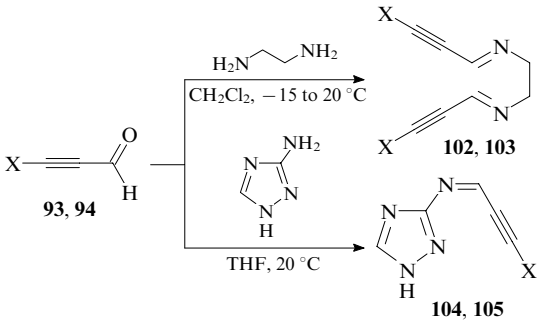
By the example of secondary phosphine chalcogenides, it was shown that the chemoselective addition of P-centred nucleophiles to the carbonyl groups in propynals **93** and **94** can efficiently proceed under mild conditions (10–50 °C, THF, without catalyst) to afford earlier unknown multifunctional chiral tertiary phosphine chalcogenides **95–101** containing ethynyl and hydroxyl functions.[290, 296]



93, **94** **95–101**

Compound	X	Y	R	Compound	X	Y	R
95	$SiMe_3$	O	Ph	**99**	$GeEt_3$	O	Ph
96	$SiMe_3$	O	2-Py	**100**	$GeEt_3$	S	Ph
97	$SiMe_3$	S	Ph	**101**	$GeEt_3$	Se	Ph
98	$SiMe_3$	Se	Ph				

The reactions of propynals **93** and **94** with ethylenediamine and 1*H*-1,2,4-triazol-3-ylamine to afford the corresponding



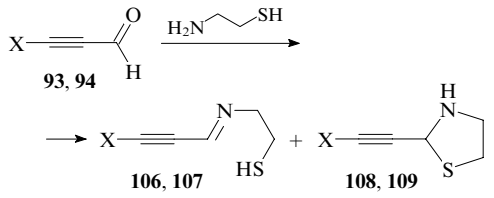
93, **94** **102**, **103**

104, **105**

X = Me_3Si (**93**, **102**, **104**), Et_3Ge (**94**, **103**, **105**).

bis(azomethines) **102**, **103** and triazolylaldimines **104**, **105** also involve the carbonyl group.[297]

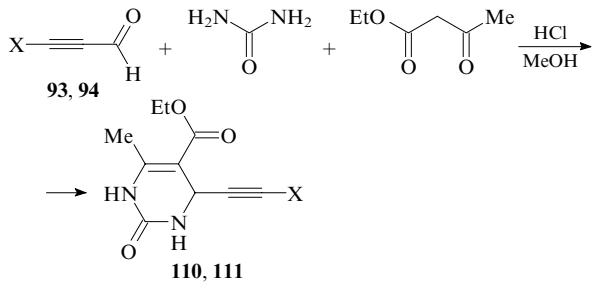
Azomethines **106**, **107** and their cyclisation products, namely, 1,3-thiazolidines **108**, **109**, were prepared from propynals **93**, **94** and 2-aminoethanethiol.[297]



X = Me_3Si (**93**, **106**, **108**), Et_3Ge (**94**, **107**, **109**).

Under microwave radiation (420 W, 12 min), the reaction can be directed to the exclusive formation of heterocycles **108**, **109**.[297]

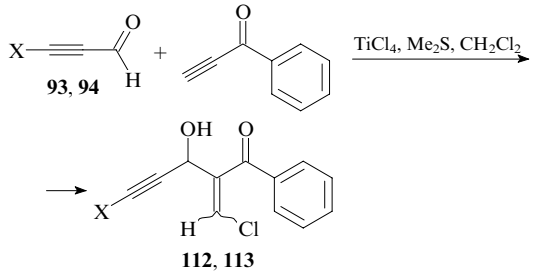
By the example of the same propynals, the possibility of using acetylenic aldehydes in the Biginelli reaction was demonstrated. Thus, on refluxing with urea and ethyl acetoacetate in methanol in the presence of HCl (5 mol %), polyfunctional tetrahydropyrimidines **110** and **111** were obtained in high yields.[298]



X = Me_3Si (**93**, **110**), Et_3Ge (**94**, **111**).

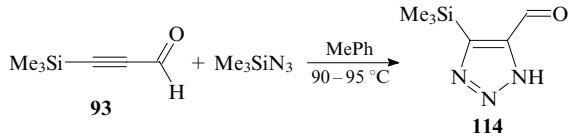
The use of $LiClO_4$ (20 mol %) instead of HCl led to the selective formation of the Knoevenagel adducts, *i.e.*, ethyl 2-acetyl-5-(trimethylsilyl)- and ethyl 2-acetyl-5-(triethylgermyl)pent-2-en-4-ynoates.[298]

Under the conditions of the Baylis–Hillman reaction ($TiCl_4$, Me_2S), propynals **93** and **94** react with 1-phenylprop-2-yn-1-one to form 3-hydroxy-1-phenyl-2-[(*Z*,*E*)-chloromethylydene]-5-X-pent-4-yn-1-ones **112**, **113**.[289]

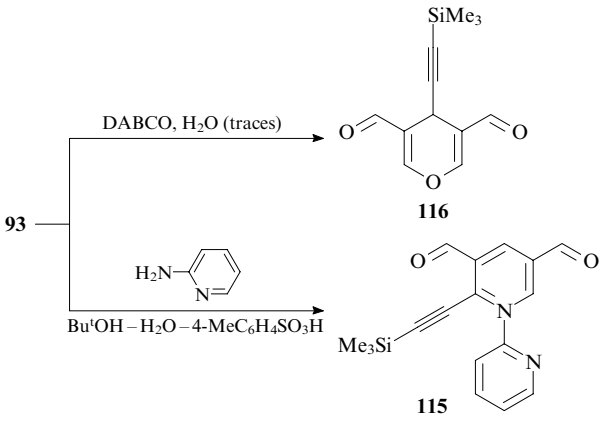


X = Me_3Si (**93**, **112**), Et_3Ge (**94**, **113**).

Regiospecific 1,3-dipolar cycloaddition of trimethylsilyl azide involves the triple bond of propynal **93** and produces 4-trimethylsilyl-1*H*-1,2,3-triazole-5-carbaldehyde (**114**).[292]

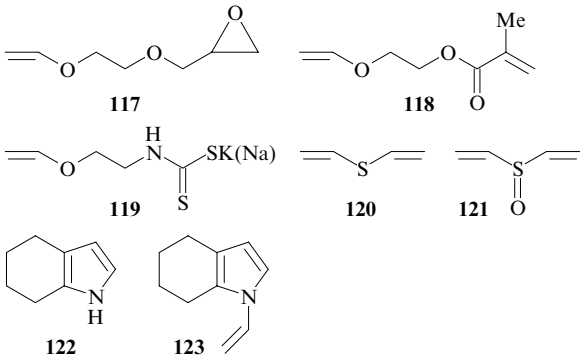


By the example of propynal **93**, unusual cascade assembling of new multifunctional heterocyclic compounds were developed. Thus under microwave radiation, the propynal **93** reacts with 2-aminopyridine in the system Bu^tOH-H_2O-4-$MeC_6H_4SO_3H$ (5 mol %) to produce *N*-(2-pyridinyl)-2-(trimethoxylylethynyl)-1,2-dihydropyridine-3,5-dicarbaldehyde (**115**) in the yield of 75%.[293] In the presence of a basic catalyst [5 mol % of diazabicyclooctane (DABCO)] and trace amounts of water, propynal **93** is quantitatively trimerised to 4-trimethylsilylethynyl-4*H*-pyran-3,5-dicarbaldehyde (**116**).[295]



VIII. New acetylene-based technologies

New modifications of classical acetylene reactions made it possible to develop simple and commercially feasible methods of the synthesis of unique monomers and intermediates that were implemented in laboratory and in pilot plants.[33] As a result, commercially feasible technologies were developed for the synthesis of pentaerythritol tetravinyl ether (**9**),[33,299–301] ethylene glycol glycidyl vinyl ether (**117**) ('Vinylox'),[53,302,303] 2-vinyloxyethyl methacrylate (**118**),[33,304,305] potassium (sodium) *N*-[2-(vinyloxy)ethyl]dithiocarbamate (biocide 'Vinditat') (**119**),[33,306] divinyl sulfide (**120**),[29,111,307] divinyl sulfoxide (**121**),[308,309] tetrahydroindole (**122**) and *N*-vinyltetrahydroindole (**123**).[30,32,310,311]



New effective methods were developed for the preparation of certain other valuable monomers and intermediates, namely, methyl vinyl and ethyl vinyl ethers,[312–314] propargyl alcohol,[99,315] *N*-vinylcarbazole,[33,316,317] 3-methylbut-1-yn-3-ol,[318,319] 1-ethynylcyclohexanol,[319] dehydrolinalool[33,320] and other acetylenic alcohols and their derivatives.[43]

Based on the developed technologies, ethylene glycol monovinyl ether (2-vinyloxyethanol),[28,33] 2-methyl-1,3-dioxolane divinyl ether,[28,33,43] diethylene glycol[28,33,160] and ethanolamine vinyl ether (2-vinyloxyethylamine)[314,321] were produced on a pilot scale ('Karbid', Temirtau).

IX. Conclusion

In this review, the progress in the studies on several classical acetylene reactions in the past 10–15 is surveyed, although it is evident that certain new modifications of these reactions rely on the achievements of earlier decades. From this review, it is evident that the interest in many directions developed by the Favorsky school is quickened. First of all, this concerns the field of base-catalysed reactions of vinylation, ethynylation and prototropic migration of a triple bond through the allene and diene structures. The systematic use of superbasic catalysts and the development of a concept of superbasicity made it possible to develop new, in principle, versions of the classical Favorsky reactions and convert them into more efficient and practically feasible synthetic methods. New processes that employ acetylene at the atmospheric or reduced pressure were carried out on the experimental and commercial scales (the vinylation of alcohols, glycols, glycerol, pentaerythritol, carbazole and ethanolamines; the preparation of divinyl sulfide; the synthesis of acetaldehyde *via* vinyl ethers).[43]

Together with the development of classical reactions, new base-catalysed reactions of acetylene, which are genetically linked to their classical prototypes, were discovered. These are the vinylation of sulfur, selenium, tellurium and phosphorus, the hydrative trimerisation of acetylene (vinylation of water), the synthesis of pyrroles and *N*-vinylpyrroles from ketones and acetylene *via* ketoximes, *etc*.[43] These reactions substantially extend the synthetic potential of acetylene.

Methods for the synthesis of macrocyclic silaalkynes that utilise the corresponding sodium and bromomagnesio derivatives of acetylene (the Iotsich complexes) were developed. Based on bis(ethynylsilanes), new unsaturated heterocyclic compounds that contain silicon and chalcogen atoms in their rings were prepared. Chemistry of silicon and germanium-containing acetylenic aldehydes has been developed further.

Some of these directions have a considerable effect on the development of the chemistry of acetylene all over the world, although, naturally, hardly embrace the whole vast field of chemistry of compounds with triple carbon–carbon bonds. The best studies carried out within the scope listed above are actively cited and many research groups successfully explore these directions.

The studies on the modification of classical acetylene reactions are in progress. In addition to superbases ($KOBu^t$) conventionally used in the synthesis of acetylenic alcohols (*e.g.*, from ferrocenylacetylene [322]), the current attention is focused on the alkynol synthesis (the addition of acetylenes to the C=O bond) in the presence of either metal complexes particularly those with chiral ligands (the asymmetric version of the Favorsky reaction),[323–326] or zinc salts and organozinc compounds,[327] triphenylphosphine,[328] organic catalysts.[329] The recently published review [330] is devoted to alkynylation of chiral aldehydes (including those with alkoxy, amino and thio groups) under the action of metal acetylides.

The addition of amines to a triple bond successfully employs the catalysis with metal complexes.[331–336] Recently, the addition of hydroselenides and diselenides to acetylenes in the presence of $InBr_3$ was accomplished.[337]

Superbases (KOH–DMSO,[338] $KOBu^t$–THF,[339] KOH–THF [340]) are successfully used in the synthesis of amides of the allene series and the corresponding propargyl compounds. The base-catalysed acetylene–allene isomerisation (acetylene 'zipper'), which employs lithium 2-aminoethylamide, is the easy way for the synthesis of 1,3-alkadiynes and their internal isomers.[341]

It should be stressed that the metal-complex catalysis now becomes the main trend in the modification of classical acetylene reactions and opens up new horizons in the traditional chemistry of acetylene;[342] however, its discussion is beyond the scope of this review.

The popularity of chemistry of acetylene increases, which is associated with the progressive extension of the use of acetylenic compounds in the organic synthesis, particularly, in the synthesis of medicinal drugs (*e.g.*, enediyne antibiotics),[343] optoelectronic materials,[344–346] molecular machines and other nanostructured objects,[27, 347] including porphyrins with acetylene bonds.

The authors hope that this review will help a wide circle of chemists and technologists in solving the topical problems of the organic synthesis and modern technologies based on the use of acetylene and its derivatives.

References

1. *Acetylene Chemistry: Chemistry, Biology, and Material Science*. (Eds F Diederich, P J Stang, R R Tykwinski) (Wiley-VCH: Weinheim, 2005)
2. R J Tedeschi *Acetylene-Based Chemicals from Coal and Other Natural Resources* (New York: Marcel Dekker, 1982)
3. L S Polak, R A Kalinenko *Neftekhimiya* **25** 271 (1985) [a]
4. H-G Beiers, H Baumann, D Bittner, J Klein, H Juntgen *Fuel* **67** 1012 (1988)
5. A M Tukhvatullin, Yu V Izinger *Tekhniko-ekonomicheskie Otsenki Plazmokhimicheskikh Protsessov Pererabotki Uglei i Uglevodorodov* (Feasibility Assessment of Plasma- Chemical Processing of Coals and Hydrocarbons) (Irkutsk: Siberian Energetic Institute, Siberian Branch of the Russian Academy of Sciences, 1989) p. 56
6. V Neverov, A Igolkin *Ekonom. Zhizn'* **41** 1 (1992)
7. B A Trofimov *Curr. Org. Chem.* **6** 1121 (2002)
8. D A Plattner, Y Li, K N Houk *Modern Acetylene Chemistry* (Eds P J Stang, F Diederich) (Weinheim: Wiley-VCH, 1995)
9. R Chauvin, C Lepetit *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 1
10. O Kitagawa, T Inoue, T Taguchi *Rev. Heteroat. Chem.* **15** 243 (1996)
11. R C Larock *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 51
12. P Aschwanden, E M Carreira *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 101
13. N J Long, C K Williams *Angew. Chem., Int. Ed.* **42** 2586 (2003)
14. U Rosenthal *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 139
15. B Bernet, A Vasella *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 173
16. R Giesa *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **C36** 631 (1996)
17. U N F Bunz *Chem. Rev.* **100** 1605 (2000)
18. T M Swager *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 233
19. D J Armitt, G T Crisp *J. Org. Chem.* **71** 3417 (2006)
20. Y Tobe, R Umeda, N Iwasa, M Sonoda *Chem.–Eur. J.* **9** 5549 (2003)
21. S Eisler, R Tykwinski *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 259
22. R B Heimann, S E Evsyukov, L Kavan *Carbyne and Carbynoid Structures* (Dordrecht: Kluwer Academic, 1999)
23. Y Tobe, T Wakabayashi *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 387
24. C Wang, A S Batsanov, M R Bryce, I Sage *Org. Lett.* **6** 2181 (2004)

25. *Metal-Catalyzed Cross-Coupling Reactions* (Eds F Diederich, P J Stang) (Weinheim: Wiely-VCH, 1998)
26. E-i Negishi, L Anastasia *Chem. Rev.* **103** 1979 (2003)
27. C S Jones, M J O'Connor, M M Haley *Acetylene Chemistry: Chemistry, Biology, and Material Science* (Eds F Diederich, P J Stang, R R Tykwinski) (Weinheim: Wiley-VCH, 2005) p. 303
28. B A Trofimov *Geteroatomnye Proizvodnye Atsetilena. Novye Polifunktsional'nye Monomery, Reagenty i Poluprodukty* (Heteroatomic Derivatives of Acetylene. New Polyfunctional Monomers, Reagents and Intermediates) (Moscow: Nauka, 1981)
29. B A Trofimov, S V Amosova *Divinilsul'fid i ego Proizvodnye* (Divinyl Sulfide and Its Derivatives) (Novosibirsk: Nauka, 1983)
30. B A Trofimov, A I Mikhaleva *N-Vinilpirroly* (*N*-Vinylpyrroles) (Novosibirsk: Nauka, 1984)
31. B A Trofimov, A G Mal'kina, Yu M Skvortsov *Zh. Org. Khim.* **29** 1268 (1993) [b]
32. B A Trofimov, A I Mikhaleva *Heterocycles* **37** 1193 (1994)
33. B A Trofimov *Zh. Org. Khim.* **31** 1368 (1995) [b]
34. B A Trofimov, A I Mikhaleva *Zh. Org. Khim.* **32** 1127 (1996) [b]
35. B Trofimov, N Gusarova, L Brandsma *Main Group Chem. News* **4** 18 (1996)
36. B A Trofimov, S N Arbuzova, N K Gusarova *Usp. Khim.* **68** 240 (1999) [*Russ. Chem. Rev.* **68** 215 (1999)]
37. S E Korostova, A I Mikhaleva, B A Trofimov *Usp. Khim.* **68** 506 (1999) [*Russ. Chem. Rev.* **68** 459 (1999)]
38. B A Trofimov, A G Mal'kina *Heterocycles* **51** 2485 (1999)
39. L N Sobenina, A P Demenev, A I Mikhaleva, B A Trofimov *Usp. Khim.* **71** 641 (2002) [*Russ. Chem. Rev.* **71** 563 (2002)]
40. B A Trofimov, L N Sobenina, A P Demenev, A I Mikhaleva *Chem. Rev.* **104** 2481 (2004)
41. B A Trofimov *Sovr. Probl. Org. Khim.* **14** 131 (2004)
42. A I Mikhaleva, A B Zaitsev, B A Trofimov *Usp. Khim.* **75** 884 (2006) [*Russ. Chem. Rev.* **75** 797 (2006)]
43. A I Mikhaleva, N K Gusarova *Atsetilen: Reaktsii i Proizvodnye (Bibliografiya Nauchnykh Trudov B A Trofimova)* [Acetylene: Reactions and Derivatives (Bibliography of Scientific Works of B A Trofimov)] (Irkutsk: Izd-vo Ottisk, 2006)
44. B A Trofimov, S V Amosova, A I Mikhaleva, N K Gusarova, E P Vyalykh *Fundamental'nye Issledovaniya. Khimicheskie Nauki* (Fundamental Research. Chemical Sciences) (Novosibirsk: Nauka, 1977) p. 174
45. B A Trofimov *Usp. Khim.* **50** 248 (1981) [*Russ. Chem. Rev.* **50** 138 (1981)]
46. B A Trofimov *Zh. Org. Khim.* **22** 1991 (1986) [b]
47. B A Trofimov, A S Atavin, V I Lavrov, M F Shostakovskii *Zh. Obshch. Khim.* **37** 743 (1967) [c]
48. USSR P. 210129; *Byull. Izobret.* (6) (1968)
49. USSR P. 1444334; *Byull. Izobret.* (46) (1988)
50. R Zimmer *Synthesis* 165 (1993)
51. O Flögel, J Dash, I Brüdgam, H Hartl, H-U Reißig *Chem. – Eur. J.* **10** 4283 (2004)
52. M A Chowdhury, H-U Ressing *Synlett* 2383 (2006)
53. B A Trofimov, N A Nedolya *Rev. Heteroat. Chem.* **9** 205 (1993)
54. D A Evans, J S Johnson *J. Am. Chem. Soc.* **120** 4895 (1998)
55. S C Ennis, A J Fairbanks, C A Slinn, R J Tennant-Eyles, H S Yeates *Tetrahedron* **57** 4221 (2001)
56. L A Oparina, O V Vysotskaya, L N Parshina, N K Gusarova, B A Trofimov *Phosphorus, Sulfur Silicon Relat. Elem.* **178** 2087 (2003)
57. B A Trofimov, B G Sukhov, S F Malysheva, N A Belogorlova, A P Tantsirev, L N Parshina, L A Oparina, S P Tunik, N K Gusarova *Tetrahedron Lett.* **45** 9143 (2004)
58. N K Gusarova, N I Ivanova, M V Bogdanova, S F Malysheva, N A Belogorlova, B G Sukhov, B A Trofimov *Mendeleev Commun.* 216 (2004)
59. B A Trofimov, L V Morozova, A I Mikhaleva, M V Markova *Vysokomol. Soedin., Ser. A* **35** 119 (1993) [d]
60. L V Morozova, A I Mikhaleva, M V Markova, B A Trofimov *Zh. Prikl. Khim.* **68** 341 (1995) [e]
61. W G S Reyntjens, E J Goethals *Polym. Adv. Technol.* **12** 107 (2001)
62. L Ding, S E Evsyukov *J. Macromol. Sci., Part A: Pure Appl. Chem.* **38** 307 (2001)
63. B A Trofimov, L V Morozova, I V Tatarinova, M Ya Khil'ko, N I Ivanova, A I Mikhaleva, T A Skotheim *Vysokomol. Soedin., Ser. A* **44** 2048 (2002) [d]
64. A I Vorob'eva, S A Onina, R R Muslukhov, S V Kolesov, L N Parshina, M Ya Khil'ko, B A Trofimov, Yu B Monakov *Vysokomol. Soedin., Ser. B* **45** 700 (2003) [d]
65. A I Vorob'eva, S A Onina, I D Musina, S V Kolesov, R R Muslukhov, L N Parshina, L A Oparina, B A Trofimov, Yu B Monakov *Vysokomol. Soedin., Ser. B* **46** 364 (2004) [d]
66. A I Vorob'eva, S A Onina, S V Kolesov, L N Parshina, L A Oparina, B A Trofimov, Yu B Monakov *Vysokomol. Soedinen., Ser. B* **46** 1239 (2004) [d]
67. B A Trofimov, L V Morozova, M V Markova, A I Mikhaleva, G F Myachina, I V Tatarinova, T A Skotheim *Vysokomol. Soedinen., Ser. B* **47** 695 (2005) [d]
68. L V Morozova, O A Tarasova, A I Mikhaleva, M V Markova, G F Myachina, B A Trofimov *Izv. Akad. Nauk, Ser. Khim.* 1958 (1997) [f]
69. O A Tarasova, L Brandsma, B A Trofimov *Synthesis* 571 (1993)
70. O A Tarasova, B A Trofimov, A I Mikhaleva, M V Sigalov, L M Sinegovskaya *Zh. Org. Khim.* **27** 1798 (1991) [b]
71. O A Tarasova, A I Mikhaleva, T L Markova, B A Trofimov *Khim. Geterotsikl. Soedin.* 125 (1992) [g]
72. O A Tarasova, T L Markova, B A Trofimov *Izv. Akad. Nauk SSSR, Ser. Khim.* 2161 (1991) [f]
73. O A Tarasova, E Yu Shmidt, L V Baikalova, A I Mikhaleva, B A Trofimov *Izv. Akad. Nauk, Ser. Khim.* 2005 (1997) [f]
74. O A Tarasova, E Yu Shmidt, L V Klyba, L M Sinegovskaya, A I Mikhaleva, L B Krivdin, B A Trofimov *Zh. Org. Khim.* **34** 730 (1998) [b]
75. M F Shostakovskii *Prostye Vinilovye Efiry* (Vinyl Ethers) (Moscow: Academy of Sciences of the USSR, 1952)
76. O A Tarasova, B A Trofimov, A V Afonin, L M Sinegovskaya, N A Kalinina, S V Amosova *Zh. Org. Khim.* **27** 1172 (1991) [b]
77. O A Tarasova, B A Trofimov, V V Keiko, S V Amosova *Zh. Org. Khim.* **27** 1180 (1991) [b]
78. B A Trofimov, A I Mikhaleva, A M Vasil'tsov, E Yu Schmidt, O A Tarasova, L V Morozova, L N Sobenina, T Preiss, J Henkelmann *Synthesis* 1125 (2000)
79. L N Parshina, Doctoral Thesis in Chemical Sciences, Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, 2005
80. A B Zaitsev, A M Vasil'tsov, E Yu Schmidt, A I Mikhaleva, L V Morozova, A V Afonin, I A Ushakov, B A Trofimov *Tetrahedron* **58** 10043 (2002)
81. B A Trofimov, S F Malysheva, N K Gusarova, A A Tatarinova, J Henkelmann *Zh. Org. Khim.* **39** 1428 (2003) [b]
82. L A Oparina, S I Shaikhudinova, L N Parshina, O V Vysotskaya, Th Preiss, J Henkelmann, B A Trofimov *Zh. Org. Khim.* **41** 672 (2005) [b]
83. L A Oparina, M Ya Khil'ko, N A Chernysheva, S I Shaikhudinova, L N Parshina, T Preiss, J Henkelmann, B A Trofimov *Zh. Org. Khim.* **41** 677 (2005) [b]
84. B A Trofimov, S F Malysheva, M V Sigalov, E P Vyalykh, G A Kalabin *Tetrahedron Lett.* **25** 4257 (1984)
85. B A Trofimov, L A Oparina, L B Krivdin, N K Gusarova, K A Chernyshev, L M Sinegovskaya, L V Klyba, L N Parshina, A P Tantsyrev, O N Kazheva, G G Alexandrov, O A D'yachenko *J. Mol. Struct.* **791** 1 (2006)
86. B A Trofimov, L A Oparina, N K Gusarova, M Ya Khil'ko, L N Parshina, J Henkelmann *Mendeleev Commun.* 13 (2006)
87. E M Carreira, W Lee, R A Singer *J. Am. Chem. Soc.* **117** 3649 (1995)
88. L F Tietze, J Gorlitzer *Synthesis* 877 (1997)
89. J M Kim, J Shin, P Shum, D H Thompson *J. Dispersion Sci. Technol.* **22** 399 (2001)
90. R T Ruck, E N Jacobsen *J. Am. Chem. Soc.* **124** 2882 (2002)
91. B A Trofimov, A M Vasil'tsov, E Yu Schmidt, A B Zaitsev, A I Mikhaleva, A V Afonin *Synthesis* 1521 (2000)
92. A B Zaitsev, A M Vasil'tsov, E Yu Shmidt, A I Mikhaleva, A V Afonin, L N Il'icheva *Zh. Org. Khim.* **39** 1479 (2003) [b]
93. B A Trofimov, O A Tarasova, A I Mikhaleva, N A Kalinina, L M Sinegovskaya, J Henkelmann *Synthesis* 1585 (2000)

94. B A Trofimov, O A Tarasova, M A Shemetova, A V Afonin, L V Klyba, L V Baikalova, A I Mikhaleva *Zh. Org. Khim.* **39** 437 (2003) [b]
95. N M Vitkovskaya, O Yu Dolgunicheva, F S Dubnikova, B A Trofimov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1339 (1988) [f]
96. N M Vitkovskaya, O Yu Dolgunicheva, F S Dubnikova, B A Trofimov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1343 (1988) [f]
97. N M Vitkovskaya, V B Kobychev, N Yu Matveenko, F S Dubnikova, O Yu Dolgunicheva, B A Trofimov *Izv. Akad. Nauk SSSR, Ser. Khim.* 1793 (1990) [f]
98. B A Trofimov, L N Sobenina, A I Mikhaleva, R N Nesterenko, M G Voronkov *Zh. Org. Khim.* **25** 1110 (1989) [b]
99. A I Moiseev, V K Stankevich, G K Balakhchi, A I Mikhaleva, R N Nesterenko, B A Trofimov *Dokl. Akad. Nauk SSSR* **321** 524 (1991) [h]
100. Russ. P. 2004542; *Byull. Izobret.* (45 – 46) (1993)
101. B A Trofimov, L N Sobenina, S E Korostova, A I Mikhaleva, N I Shishov, V D Fel'dman, S G Shevchenko, A N Vasil'ev *Zh. Prikl. Khim.* **60** 1366 (1987) [e]
102. V K Stankevich, G R Klimenko, B F Kukharev, B A Trofimov *Zh. Prikl. Khim.* **73** 163 (2000) [e]
103. B A Trofimov, E P Vyalykh, S F Malysheva *Zh. Org. Khim.* **12** 2469 (1976) [e]
104. USSR P. 633856; *Byull. Izobret.* (43) (1978)
105. B A Trofimov, S N Istomina, S F Malysheva, E P Vyalykh *Izv. Akad. Nauk SSSR, Ser. Khim.* 2402 (1978) [f]
106. B A Trofimov, S F Malysheva, E P Vyalykh *Zh. Org. Khim.* **15** 880 (1979) [b]
107. B A Trofimov, S V Amosova, M L Al'pert, O A Tarasova *Zh. Org. Khim.* **13** 2230 (1977) [b]
108. B A Trofimov *Z. Chem.* **26** 41 (1986)
109. N K Gusarova, B A Trofimov, A S Atavin, S V Amosova, A V Gusarov *Zh. Org. Khim.* **7** 1780 (1971) [b]
110. USSR P. 387982; *Byull. Izobret.* (28) (1973)
111. B A Trofimov *Sulfur Rep.* **11** 207 (1992)
112. V A Potapov, S V Amosova, V Yu Shestakova, A A Starkova, A R Zhnikin *Sulfur Lett.* **21** 105 (1997)
113. USSR P. 568638; *Byull. Izobret.* (30) (1977)
114. B A Trofimov, S V Amosova, N K Gusarova, G K Musorin *Tetrahedron* **38** 713 (1982)
115. N K Gusarova, A A Tatarinova, L M Sinegovskaya *Sulfur Rep.* **11** 1 (1991)
116. B A Trofimov, T N Rakhmatulina, N K Gusarova, S F Malysheva *Usp. Khim.* **60** 2619 (1991) [*Russ. Chem. Rev.* **60** 1360 (1991)]
117. N K Gusarova, S F Malysheva, S N Arbuzova, B A Trofimov *Izv. Akad. Nauk, Ser. Khim.* 1695 (1998) [f]
118. B G Sukhov, N K Gusarova, S F Malysheva, B A Trofimov *Izv. Akad. Nauk, Ser. Khim.* 1172 (2003) [f]
119. S F Malysheva, S N Arbuzova *Sovremennyi Organicheskii Sintez* (Modern Organic Synthesis) (Moscow: Khimiya, 2003) p. 160
120. B A Trofimov, B G Sukhov, S F Malysheva, N K Gusarova *Kat. Prom-sti* (4) 18 (2006)
121. B A Trofimov, A I Mikhaleva, A N Vasil'ev, M V Sigalov *Izv. Akad. Nauk SSSR, Ser. Khim.* 695 (1979) [f]
122. BRD P. 19834654; *Chem. Abstr.* **132** 109750 (2000)
123. A M Vasil'tsov, Doctoral Thesis in Chemical Sciences, Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, 2001
124. E Yu Shmidt, Doctoral Thesis in Chemical Sciences, Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, 2005
125. B A Trofimov, E Yu Schmidt, A I Mikhaleva, A M Vasil'tsov, A V Afonin *Mendeleev Commun.* 29 (2000)
126. B A Trofimov, E Yu Schmidt, A M Vasil'tsov, A I Mikhaleva, A B Zaitsev, L V Morozova, A G Gorshkov, J Henkelmann, J-D Arndt *Synthesis* 2427 (2001)
127. B A Trofimov *Adv. Heterocycl. Chem.* **51** 177 (1990)
128. B A Trofimov, S E Korostova, S G Shevchenko, E A Polubentsev, A I Mikhaleva *Zh. Org. Khim.* **26** 1110 (1990) [b]
129. B A Trofimov *The Chemistry of Heterocyclic Compounds. Pyrroles* (Ed. R A Jones) (New York: Wiley-Interscience, 1992) Vol. 48, Pt. 2, p. 131
130. B A Trofimov, L V Sokolyanskaya, R N Kudyakova *Sulfur Lett.* **18** 27 (1994)
131. B A Trofimov, A M Vasil'tsov, E Yu Shmidt, O V Petrova, A I Mikhaleva *Zh. Org. Khim.* **30** 576 (1994) [b]
132. O V Petrova, A I Mikhaleva, L N Sobenina, E Yu Schmidt, E I Kositsyna *Mendeleev Commun.* 162 (1997)
133. O V Petrova, A I Mikhaleva, L N Sobenina, E Yu Shmidt, E I Kositsina *Zh. Org. Khim.* **33** 1078 (1997) [b]
134. A M Vasil'tsov, E Yu Shmidt, A I Mikhaleva, A V Afonin, A B Zaitsev *Khim. Geterotsikl. Soedin.* 1641 (2001) [g]
135. A M Vasil'tsov, A B Zaitsev, E Yu Schmidt, A I Mikhaleva, A V Afonin *Mendeleev Commun.* 74 (2001)
136. A M Vasil'tsov, A B Zaitsev, A I Mikhaleva, E Yu Shmidt, A V Afonin *Khim. Geterotsikl. Soedin.* 66 (2002) [g]
137. A B Zaitsev, Candidate Thesis in Chemical Sciences, Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, 2003
138. B A Trofimov, A B Zaitsev, E Yu Schmidt, A M Vasil'tsov, A I Mikhaleva, I A Ushakov, A V Vashchenko, N V Zorina *Tetrahedron Lett.* **45** 3789 (2004)
139. E Yu Schmidt, N V Zorina, A B Zaitsev, A I Mikhaleva, A M Vasil'tsov, P Audebert, G Clavier, R Méallet-Renault, R B Pansu *Tetrahedron Lett.* **45** 5489 (2004)
140. A B Zaitsev, R Méallet-Renault, E Yu Schmidt, A I Mikhaleva, S Badré, C Dumas, A M Vasil'tsov, N V Zorina, R B Pansu *Tetrahedron* **61** 2683 (2005)
141. A M Vasil'tsov, E Yu Schmidt, A I Mikhaleva, N V Zorina, A B Zaitsev, O V Petrova, L B Krivdin, K B Petrushenko, I A Ushakov, C Pozo-Conzalo, J A Pomposo, H-J Grande *Tetrahedron* **61** 7756 (2005)
142. B A Trofimov, A M Vasil'tsov, E Yu Schmidt, N V Zorina, A V Afonin, A I Mikhaleva, K B Petrushenko, I A Ushakov, L B Krivdin, V K Belsky, L I Bryukvina *Eur. J. Org. Chem.* 4338 (2005)
143. E Yu Schmidt, A I Mikhaleva, A M Vasil'tsov, A B Zaitsev, N V Zorina *Arkivoc* (vii) 11 (2005)
144. A B Zaitsev, E Yu Shmidt, A M Vasil'tsov, A I Mikhaleva, A V Afonin, I A Ushakov *Khim. Geterotsikl. Soedin.* 839 (2005) [g]
145. A I Mikhaleva, E Yu Shmidt *Izbrannye Metody Sinteza i Modifikatsii Geterotsiklov* (Selected Methods of Synthesis and Modification of Heterocycles) (Moscow: IBS Press, 2003) Vol. 1, p. 349
146. A B Zaitsev, E Yu Shmidt, A M Vasil'tsov, A I Mikhaleva, O V Petrova, A V Afonin, N V Zorina *Khim. Geterotsikl. Soedin.* 39 (2006) [g]
147. A F Pozharskii, V A Anisimova, E B Tsupak *Prakticheskie Raboty po Khimii Geterotsiklov* (Practical Works on the Chemistry of Heterocycles) (Rostov: Rostov University, 1988) p. 159
148. G P Bean *The Chemistry of Heterocyclic Compounds. Pyrroles* (Ed. R A Jones) (New York: Wiley-Interscience, 1992) Vol. 48, Pt. 2, p. 105
149. R J Tedeschi *Encyclopedia of Physical Science and Technology* Vol. 1 (San Diego, CA: Academic Press, 1992) p. 27
150. A Gossauer *Methoden der Organischen Chemie. Hetarene I. (Houben-Weyl)* Teil 1 (Stuttgart, New York: Georg Thieme, 1994) p. 556
151. M Puciova, P Ertl, S Toma *Collect. Czech. Chem. Commun.* **59** 175 (1994)
152. A V Varlamov, L G Voskresenskii, T N Borisova, A I Chernyshev, A N Levov *Khim. Geterotsikl. Soedin.* 683 (1999) [g]
153. J Chen, A Burghart, A Derecskei-Kovacs, K Burgess *J. Org. Chem.* **65** 2900 (2000)
154. E Abele, E Lukevics *Heterocycles* **53** 2285 (2000)
155. T L Gilchrist *J. Chem. Soc., Perkin Trans. 1* 2491 (2001)
156. L-X Wang, X-G Li, Y-L Yang *React. Funct. Polym.* **47** 125 (2001)
157. E Abele, E Lukevits *Khim. Geterotsikl. Soedin.* 156 (2001) [g]

158. B A Trofimov, E Yu Schmidt, A I Mikhaleva, N V Zorina, I A Ushakov, A V Afonin, A M Vasil'tsov *Mendeleev Commun.* 40 (2007)
159. B A Trofimov, L A Oparina, L N Parshina, V V Vins, V I Lavrov *Izv. Akad. Nauk SSSR, Ser. khim.* 2873 (1989) [f]
160. B A Trofimov, R N Kudyakova, L A Oparina, L N Parshina, V V Vins *Zh. Prikl. Khim.* **64** 873 (1991) [e]
161. B A Trofimov, A G Mal'kina, A V Afonin, I A Ushakov, V V Nosyreva, V K Bel'skii *Zh. Org. Khim.* **39** 1430 (2003) [b]
162. B A Trofimov, O A Tarasova, M V Sigalov, A I Mikhaleva *Tetrahedron Lett.* **36** 9181 (1995)
163. O A Tarasova, E Yu Shmidt, L M Sinegovskaya, O V Petrova, L N Sobenina, A I Mikhaleva, L Brandsma, B A Trofimov *Zh. Org. Khim.* **35** 1614 (1999) [b]
164. B A Trofimov, Yu M Skvortsov, E I Moshchevitina, A G Mal'kina, V K Bel'skii *Zh. Org. Khim.* **25** 221 (1989) [b]
165. B A Trofimov, Yu M Skvortsov, A G Mal'kina, A I Gritsa *Sulfur Lett.* **11** 209 (1990)
166. B A Trofimov, A G Mal'kina, Yu M Skvortsov, V K Bel'ski, E I Moshchevitina *Sulfur Lett.* **13** 63 (1991)
167. A G Mal'kina, Yu M Skvortsov, E I Moshchevitina, V K Bel'skii, B A Trofimov *Khim. Geterotsikl. Soedin.* 335 (1992) [g]
168. B A Trofimov, L V Andriankova, A G Mal'kina, A V Afonin, T I Vakul'skaya *Sulfur Lett.* **20** 23 (1996)
169. A G Mal'kina, E I Moshchevitina, Yu M Skvortsov, L V Sokolyanskaya, B A Trofimov *Zh. Org. Khim.* **35** 1637 (1999) [b]
170. A G Mal'kina, R N Kudyakova, B A Trofimov *Zh. Org. Khim.* **37** 737 (2001) [b]
171. B A Trofimov, A G Mal'kina, O A Shemyakina, R N Kudyakova, L V Sokolyanskaya, L M Sinegovskaya, A I Albanov, V I Smirnov, O N Kazheva, A N Chekhlov, O A D'yachenko *Zh. Org. Khim.* **41** 903 (2005) [b]
172. A G Mal'kina, O A Shemyakina, V V Nosyreva, A I Albanov, L V Klyba, E R Zhanchipova, B A Trofimov *Synthesis* 637 (2006)
173. Yu M Skvortsov, O M Fartysheva, A G Mal'kina, B A Trofimov *Khim. Geterotsikl. Soedin.* 1689 (1985) [g]
174. Yu M Skvortsov, O M Fartysheva, A G Mal'kina, E I Kositsyna, T V Kashik, S M Ponomareva, M V Sigalov, B A Trofimov *Zh. Org. Khim.* **22** 255 (1986) [b]
175. Yu M Skvortsov, A G Mal'kina, O M Fartysheva, M V Sigalov, B A Trofimov *Zh. Org. Khim.* **22** 260 (1986) [b]
176. B A Trofimov, A G Mal'kina, Yu M Skvortsov, L V Sokolyanskaya, V I Smirnov, E I Kositsyna *Dokl. Akad. Nauk SSSR* **318** 1395 (1991) [h]
177. B A Trofimov, A G Mal'kina, Yu M Skvortsov, L V Sokolyanskaya, V I Smirnov, E I Kositsyna *Zh. Org. Khim.* **28** 881 (1992) [b]
178. A G Mal'kina, L V Sokolyanskaya, R N Kudyakova, L M Sinegovskaya, A I Albanov, O A Shemyakina, B A Trofimov *Zh. Org. Khim.* **41** 64 (2005) [b]
179. B A Trofimov, L V Andriyankova, S A Zhivet'ev, A G Mal'kina, V K Voronov *Tetrahedron Lett.* **43** 1093 (2002)
180. B A Trofimov, L V Andriyankova, S I Shaikhudinova, T I Kazantseva, A G Mal'kina, S A Zhivet'ev, A V Afonin *Synthesis* 853 (2002)
181. L V Andriyankova, A G Mal'kina, A V Afonin, B A Trofimov *Mendeleev Commun.* 186 (2003)
182. L V Andriyankova, A G Mal'kina, L P Nikitina, K V Belyaeva, I A Ushakov, A V Afonin, M V Nikitin, B A Trofimov *Tetrahedron* **61** 8031 (2005)
183. B A Trofimov, L V Andriyankova, R T Tlegenov, A G Mal'kina, A V Afonin, L N Il'icheva, L P Nikitina *Mendeleev Commun.* 33 (2005)
184. B A Trofimov, L V Andriyankova, A G Mal'kina, L P Nikitina, A V Afonin, I A Ushakov, L M Sinegovskaya, T I Vakul'skaya *Eur. J. Org. Chem.* 1581 (2006)
185. B A Trofimov, L V Andriyankova, A G Mal'kina, K V Belyaeva, L P Nikitina, O A Dyachenko, O N Kazheva, A N Chekhlov, G V Shilov, A V Afonin, I A Ushakov, L V Baikalova *Eur. J. Org. Chem.* 1018 (2007)
186. A G Mal'kina, R Besten, A C H T M Kerk, L Brandsma, B A Trofimov *J. Organomet. Chem.* **493** 271 (1995)
187. B A Trofimov, L Brandsma, S N Arbuzova, N K Gusarova *Zh. Obshch. Khim.* **67** 343 (1997) [c]
188. B A Trofimov, L Brandsma, S N Arbuzova, N K Gusarova *Izv. Akad. Nauk, Ser. Khim.* 884 (1997) [f]
189. B A Trofimov *J. Heterocycl. Chem.* **36** 1469 (1999)
190. S N Arbuzova, L Brandsma, N K Gusarova, M V Nikitin, B A Trofimov *Mendeleev Commun.* 66 (2000)
191. L Brandsma, N A Nedolya, O A Tarasova, B A Trofimov *Khim. Geterotsikl. Soedin.* 1443 (2000) [g]
192. L Brandsma, N A Nedolya *Synthesis* 735 (2004)
193. N A Nedolya, L Brandsma, B A Trofimov *Dokl. Akad. Nauk* **350** 68 (1996) [h]
194. L Brandsma, N A Nedolya, R-J Lang, B A Trofimov *Izv. Akad. Nauk, Ser. Khim.* 3024 (1996) [f]
195. N A Nedolya, R-J Lang, L Brandsma, B A Trofimov *Zh. Org. Khim.* **33** 87 (1997) [b]
196. N A Nedolya, L Brandsma, R-J Lang, B A Trofimov *Zh. Org. Khim.* **33** 637 (1997) [b]
197. N A Nedolya, L Brandsma, R-J Lang, B A Trofimov *Zh. Org. Khim.* **33** 1437 (1997) [b]
198. L Brandsma, N A Nedolya, R-J Lang, B A Trofimov *Khim. Geterotsikl. Soedin.* 571 (1997) [g]
199. L Brandsma, N A Nedolya, V Heerma, A C H T M Kerk, E T H G Lutz, R-J Lang, A V Afonin, B A Trofimov *Khim. Geterotsikl. Soedin.* 572 (1997) [g]
200. L Brandsma, N A Nedolya, O A Tarasova, L V Klyba, L M Sinegovskaya, B A Trofimov *Dokl. Akad. Nauk* **357** 350 (1997) [h]
201. L Brandsma, N A Nedolya, H D Verkruijsse, N L Owen, L Du, B A Trofimov *Tetrahedron Lett.* **38** 6905 (1997)
202. O A Tarasova, N A Nedolya, V Yu Vvedensky, L Brandsma, B A Trofimov *Tetrahedron Lett.* **38** 7241 (1997)
203. L Brandsma, N A Nedolya, O A Tarasova, L V Klyba, L M Sinegovskaya, B A Trofimov *Zh. Org. Khim.* **35** 953 (1999) [b]
204. L Brandsma, N A Nedolya, B A Trofimov *Eur. J. Org. Chem.* 2663 (1999)
205. B A Trofimov, A I Mikhaleva, L V Morozova *Usp. Khim.* **54** 1034 (1985) [*Russ. Chem. Rev.* **54** 609 (1985)]
206. B A Trofimov *Phosphorus, Sulfur Silicon Relat. Elem.* **95 – 96** 145 (1994)
207. B A Trofimov, M V Sigalov *Main Group Chem. News* **6** 30 (1998)
208. B A Trofimov *Khimiya i Biologicheskaya Aktivnost' Sinteticheskikh i Prirodnykh Soedinenii. Kislorod- i Serusoderzhashchie Geterotsikly* (The Chemistry and Biological Activity of Synthetic and Natural Compounds. Oxygen- and Sulfur-containing Heterocycles) (Moscow: IBS Press, 2003) Vol. 1, p. 119
209. B A Trofimov, L N Sobenina, A I Mikhaleva, M P Sergeeva, N I Golovanova, R I Polovnikova, A N Vavilova *Khim. Geterotsikl. Soedin.* 1176 (1992) [g]
210. B A Trofimov, L N Sobenina, A I Mikhaleva, M P Sergeeva, R I Polovnikova *Sulfur Lett.* **15** 219 (1992)
211. L N Sobenina, L E Protasova, M P Sergeeva, O V Petrova, T N Aksamentova, O B Kozyreva, R I Polovnikova, A I Mikhaleva, B A Trofimov *Khim. Geterotsikl. Soedin.* 47 (1995) [g]
212. B A Trofimov, L N Sobenina, A I Mikhaleva, A P Demenev, O A Tarasova, I A Ushakov, S V Zinchenko *Tetrahedron* **56** 7325 (2000)
213. B A Trofimov, L N Sobenina, A I Mikhaleva, M P Sergeeva, N I Golovanova *Zh. Org. Khim.* **28** 1766 (1992) [b]
214. L N Sobenina, A I Mikhaleva, M P Sergeeva, O V Petrova, T N Aksamentova, O B Kozyreva, D-S D Toryashinova, B A Trofimov *Tetrahedron* **51** 4223 (1995)
215. B A Trofimov, A P Demenev, L N Sobenina, A I Mikhaleva, O A Tarasova *Tetrahedron Lett.* **44** 3501 (2003)
216. A P Demenev, L N Sobenina, A I Mikhaleva, B A Trofimov *Sulfur Lett.* **26** 95 (2003)

217. B A Trofimov, L N Sobenina, A I Mikhaleva, M P Sergeeva, M V Sigalov, N I Golovanova *Khim. Geterotsikl. Soedin*. 998 (1992) [g]
218. L I Sobenina, A I Mikhaleva, M P Sergeeva, D-S D Toryashinova, O B Kozyreva, B A Trofimov *Khim. Geterotsikl. Soedin*. 919 (1996) [g]
219. L N Sobenina, A I Mikhaleva, D-S D Toryashinova, O B Kozyreva, B A Trofimov *Sulfur Lett*. **20** 205 (1997)
220. L N Sobenina, A I Mikhaleva, B A Trofimov *Khim. Geterotsikl. Soedin*. 418 (1995) [g]
221. L N Sobenina, A I Mikhaleva, D-S D Toryashinova, B A Trofimov *Sulfur Lett*. **20** 9 (1996)
222. L N Sobenina, A I Mikhaleva, B A Trofimov *Ross. Khim. Zh*. **49** (6) 97 (2005) [i]
223. B A Trofimov, O V Petrova, L N Sobenina, V N Drichkov, A I Mikhaleva, I A Ushakov, O A Tarasova, O N Kazheva, A N Chekhlov, O A Dyachenko *Tetrahedron* **62** 4146 (2006)
224. B A Trofimov, O V Petrova, L N Sobenina, I A Ushakov, A I Mikhaleva, Yu Yu Rusakov, L B Krivdin *Tetrahedron Lett*. **47** 3645 (2006)
225. B A Trofimov, E Yu Schmidt, A I Mikhaleva, A M Vasil'tsov, A B Zaitsev, N S Smolyanina, E Yu Senotrusova, A V Afonin, I A Ushakov, K B Petrushenko, O N Kazheva, O A Dyachenko, V V Smirnov, A F Schmidt, M V Markova, L V Morozova *Eur. J. Org. Chem*. 4021 (2006)
226. Yu Yu Rusakov, L B Krivdin, E Yu Senotrusova, E Yu Schmidt, A M Vasiltsov, A I Mikhaleva, B A Trofimov, O A Dyachenko, A N Chekhlov, O N Kazheva *Magn. Reson. Chem*. **45** 142 (2007)
227. A I Mikhaleva, A B Zaitsev, A V Ivanov, E Yu Schmidt, A M Vasil'tsov, B A Trofimov *Tetrahedron Lett*. **47** 3693 (2006)
228. A M Vasiltsov, A V Ivanov, I A Ushakov, A I Mikhaleva, B A Trofimov *Synthesis* 452 (2007)
229. B G Sukhov, S F Malysheva, T I Vakul'skaya, V V Tirsky, E F Martynovich, Yu V Smetannikov, N P Tarasova *Arkivoc* (xiii) 196 (2003)
230. B A Trofimov, L Brandsma, S N Arbuzova, S F Malysheva, N K Gusarova *Tetrahedron Lett*. **35** 7647 (1994)
231. S N Arbuzova, L Brandsma, N K Gusarova, B A Trofimov *Recl. Trav. Chim. Pays-Bas* **113** 575 (1994)
232. L Brandsma, N K Gusarova, A V Gusarov, H D Verkruijsse, B A Trofimov *Synth. Commun*. **24** 3219 (1994)
233. L Brandsma, J A Doorn, R-J Lang, N K Gusarova, B A Trofimov *Mendeleev Commun*. 14 (1995)
234. B A Trofimov, N K Gusarova, L Brandsma *Phosphorus, Sulfur Silicon Relat. Elem*. **109** – **110** 601 (1996)
235. S N Arbuzova, N K Gusarova, S F Malysheva, L Brandsma, A I Albanov, B A Trofimov *Zh. Obshch. Khim*. **66** 56 (1996) [c]
236. B A Trofimov, S I Shaikhudinova, V I Dmitriev, K V Nepomnyashchikh, T I Kazantseva, N K Gusarova *Zh. Obshch. Khim*. **70** 43 (2000) [c]
237. N K Gusarova, S I Shaikhudinova, T I Kazantseva, S F Malysheva, B G Sukhov, N A Belogorlova, V I Dmitriev, B A Trofimov *Zh. Obshch. Khim*. **72** 399 (2002) [c]
238. N K Gusarova, M V Bogdanova, N I Ivanova, N A Chernysheva, B G Sukhov, L M Sinegovskaya, O N Kazheva, G G Alexandrov, O A D'yachenko, B A Trofimov *Synthesis* 3103 (2005)
239. B G Sukhov, N K Gusarova, N I Ivanova, M V Bogdanova, O N Kazheva, G G Aleksandrov, O A D'yachenko, L M Sinegovskaya, S F Malysheva, B A Trofimov *Zh. Strukt. Khim*. **46** 1103 (2005) [j]
240. S N Arbuzova, N K Gusarova, B A Trofimov *Arkivoc* (v) 12 (2006)
241. N K Gusarova, S F Malysheva, S N Arbuzova, L Brandsma, B A Trofimov *Zh. Obshch. Khim*. **64** 2062 (1994) [c]
242. B A Trofimov, N K Gusarova, S N Arbuzova, S F Malysheva, R Besten, L Brandsma *Synthesis* 387 (1995)
243. N Gusarova, L Brandsma, S Malysheva, S Arbuzova, B Trofimov *Phosphorus, Sulfur Silicon Relat. Elem*. **111** 174 (1996)
244. S F Malysheva, B G Sukhov, L I Larina, N A Belogorlova, N K Gusarova, B A Trofimov *Zh. Obshch. Khim*. **71** 2012 (2001) [c]
245. N K Gusarova, S I Shaikhudinova, S N Arbuzova, T I Vakul'skaya, B G Sukhov, L M Sinegovskaya, M V Nikitin, A G Mal'kina, N A Chernysheva, B A Trofimov *Tetrahedron* **59** 4789 (2003)
246. B A Trofimov, S N Arbuzova, A G Mal'kina, N K Gusarova, S F Malysheva, M V Nikitin, T I Vakul'skaya *Mendeleev Commun*. 163 (1999)
247. S N Arbuzova, S I Shaikhudinova, N K Gusarova, M V Nikitin, A G Mal'kina, B G Sukhov, M V Bogdanova, B A Trofimov *Zh. Obshch. Khim*. **75** 552 (2005) [c]
248. B A Trofimov, B G Sukhov, S F Malysheva, N A Belogorlova, S N Arbuzova, S P Tunik, N K Gusarova *Zh. Org. Khim*. **40** 138 (2004) [b]
249. S N Arbuzova, N K Gusarova, M V Bogdanova, N I Ivanova, I A Ushakov, A G Mal'kina, B A Trofimov *Mendeleev Commun*. 183 (2005)
250. M G Voronkov, O G Yarosh, G Yu Turkina, V Yu Vitkovskii, A I Albanov *J. Organomet. Chem*. **389** 1 (1990)
251. M G Voronkov, O G Yarosh, V K Roman, A I Albanov *Metalloorg. Khim*. **3** 1423 (1990) [k]
252. Yu E Ovchinnikov, V A Igonin, I A Zamaev, V E Shklover, Yu T Struchkov, O G Yarosh, M G Voronkov, G Yu Turkina *Zh. Strukt. Khim*. **32** 116 (1991) [j]
253. Yu E Ovchinnikov, V A Igonin, I A Zamaev, V E Shklover, Yu T Struchkov, O G Yarosh, M G Voronkov, G Yu Turkina, T M Orlova *Metalloorg. Khim*. **4** 1011 (1991) [k]
254. M Voronkov, O Yarosh, L Zhilitskaya *Phosphorus, Sulfur Silicon Relat. Elem*. **65** 33 (1992)
255. Yu E Ovchinnikov, Yu T Struchkov, M G Voronkov, O G Yarosh, G Yu Turkina, T M Orlova *Metalloorg. Khim*. **5** 1280 (1992) [k]
256. Yu E Ovchinnikov, Yu T Struchkov, O G Yarosh, G Yu Turkina, M G Voronkov *Zh. Strukt. Khim*. **34** 139 (1993) [j]
257. M G Voronkov, O G Yarosh, L V Zhilitskaya, A I Albanov, V Yu Vitkovskii *Metalloorg. Khim*. **6** 77 (1993) [k]
258. O G Yarosh, L V Zhilitskaya, A I Albanov, L V Klyba, M G Voronkov *Zh. Obshch. Khim*. **64** 281 (1994) [c]
259. O G Yarosh, L V Zhilitskaya, A I Albanov, L V Klyba, M G Voronkov *Zh. Obshch. Khim*. **64** 1801 (1994) [c]
260. O G Yarosh, L V Zhilitskaya, A I Albanov, T D Burnashova, M G Voronkov *Zh. Obshch. Khim*. **65** 609 (1995) [c]
261. O G Yarosh, M G Voronkov, E I Brodskaya *Usp. Khim*. **64** 896 (1995) [*Russ. Chem. Rev*. **64** 839 (1995)]
262. M G Voronkov, L V Zhilitskaya, O G Yarosh, A I Albanov, L V Klyba *Zh. Obshch. Khim*. **67** 2006 (1997) [c]
263. L V Zhilitskaya, O G Yarosh, A I Albanov, L V Klyba, T D Burnashova, M G Voronkov *Zh. Obshch. Khim*. **69** 1456 (1999) [c]
264. M G Voronkov, O G Yarosh, L V Zhilitskaya, A I Albanov *Zh. Obshch. Khim*. **70** 1650 (2000) [c]
265. M G Voronkov, L V Zhilitskaya, O G Yarosh, T D Burnashova, A I Albanov, L V Klyba *Zh. Obshch. Khim*. **71** 578 (2001) [c]
266. O G Yarosh, V V Bystrova, A I Albanov, L V Klyba, M G Voronkov *Zh. Obshch. Khim*. **71** 1974 (2001) [c]
267. O G Yarosh, L V Zhilitskaya, N K Yarosh, A I Albanov, M G Voronkov *Zh. Obshch. Khim*. **73** 1645 (2003) [c]
268. O G Yarosh, L V Zhilitskaya, N K Yarosh, A I Albanov, L V Klyba, M G Voronkov *Zh. Obshch. Khim*. **74** 1282 (2004) [c]
269. O G Yarosh, L V Zhilitskaya, N K Yarosh, E E Istomina, A I Albanov, Yu A Chuvashev, M G Voronkov *Zh. Obshch. Khim*. **74** 1612 (2004) [c]
270. O G Yarosh, L V Zhilitskaya, E E Istomina, N K Yarosh, A I Albanov, M G Voronkov *Zh. Obshch. Khim*. **75** 1157 (2005) [c]
271. O G Yarosh, L V Zhilitskaya, N K Yarosh, A I Albanov, M G Voronkov *Zh. Obshch. Khim*. **75** 1299 (2005) [c]
272. L V Zhilitskaya, E E Istomina, O G Yarosh, M G Voronkov *Zh. Obshch. Khim*. **76** 1315 (2006) [c]

273. L V Zhilitskaya, E E Istomina, N K Yarosh, M G Voronkov, A I Albanov, O G Yarosh *Zh. Obshch. Khim.* **76** 1952 (2006) [c]
274. V A Potapov, S V Amosova, O V Belozerova, A I Albanov, O G Yarosh, M G Voronkov *Khim. Geterotsikl. Soedin.* 633 (2003) [g]
275. V A Potapov, S V Amosova, O V Belozerova, A I Albanov, O G Yarosh, M G Voronkov *Khim. Geterotsikl. Soedin.* 634 (2003) [g]
276. L V Klyba, S V Amosova, O V Belozerova, V A Potapov, E R Zhanchipova, O G Yarosh, M G Voronkov *Izv. Akad. Nauk, Ser. Khim.* 639 (2005) [f]
277. O V Belozerova, Candidate Thesis in Chemical Sciences, Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Irkutsk, 2006
278. M M Demina, A A Velikanov, A S Medvedeva, M G Voronkov *Zh. Obshch. Khim.* **63** 2274 (1993) [c]
279. A S Medvedeva, V V Novokshonov, M M Demina, M G Voronkov *Zh. Obshch. Khim.* **64** 1224 (1994) [c]
280. V V Novokshonov, A S Medvedeva, M M Demina, L V Sherstyannikova, M G Voronkov *Zh. Org. Khim.* **32** 1828 (1996) [b]
281. M M Demina, A A Velikanov, A S Medvedeva, M G Voronkov *J. Organomet. Chem.* **553** 129 **(**1998)
282. A S Medvedeva, V V Novokshonov, M M Demina, M G Voronkov *J. Organomet. Chem.* **553** 481 **(**1998)
283. A S Medvedeva, I A Yazovtsev, L P Safronova, M M Demina *Zh. Org. Khim.* **34** 141 (1998) [b]
284. A S Medvedeva, V V Novokshonov *Zh. Org. Khim.* **34** 1412 (1998) [b]
285. V V Novokshonov, A S Medvedeva, A V Mareev *Zh. Org. Khim.* **37** 626 (2001) [b]
286. A S Medvedeva, A V Mareev, A I Borisova, A V Afonin *Arkivoc* (xiii) 157 (2003)
287. A V Mareev, A S Medvedeva, A V Khatashkeev, A V Afonin *Mendeleev Commun.* 263 (2005)
288. A S Medvedeva *Zh. Org. Khim.* **32** 289 (1996) [b]
289. A S Medvedeva, M M Demina, P S Novopashin, G I Sarapulova, A V Afonin *Mendeleev Commun.* 110 (2002)
290. N K Gusarova, A M Reutskaya, N I Ivanova, A S Medvedeva, M M Demina, P S Novopashin, A V Afonin, A I Albanov, B A Trofimov *J. Organomet. Chem.* **659** 172 (2002)
291. A S Medvedeva, V V Novokshonov, A V Mareev, A I Borisova *Zh. Org. Khim.* **39** 368 (2003) [b]
292. M M Demina, P S Novopashin, G I Sarapulova, L I Larina, A S Smolin, V S Fundamenskii, A A Kashaev, A S Medvedeva *Zh. Org. Khim.* **40** 1852 (2004) [b]
293. A S Medvedeva, A V Mareev, A V Afonin, I A Ushakov *Zh. Org. Khim.* **41** 478 (2005) [b]
294. A V Mareev, A V Tikhonov, A V Afonin, I A Ushakov, A S Medvedeva *Zh. Org. Khim.* **41** 1425 (2005) [b]
295. A S Medvedeva, A V Khatashkeev, A V Mareev, A V Afonin, I A Ushakov *Zh. Org. Khim.* **41** 1740 (2005) [b]
296. N K Gusarova, N I Ivanova, N A Konovalova, B G Sukhov, L V Balkalova, L M Sinegovskaya, D V Pavlov, B A Trofimov *Synthesis* 4159 (2006)
297. M M Demina, P S Novopashin, T V Kon'kova, G I Sarapulova, A V Afonin, A S Medvedeva *Khim. Geterotsikl. Soedin.* 1697 (2006) [g]
298. V V Novokshonov, I A Novokshonova, I A Ushakov, A S Medvedeva *Khim. Geterotsikl. Soedin.* 1734 (2006) [g]
299. Russ. P. 1504968; *Byull. Izobret.* (21) (1994)
300. B A Trofimov, S F Malysheva, E P Vyalykh, L M Sinegovskaya, N K Gusarova *Zh. Org. Khim.* **34** 507 (1998) [b]
301. B A Trofimov, S F Malysheva *Nauka — Proizvodstvu* (6) 12 (2003)
302. USSR P. 1129208; *Byull. Izobret.* (46) (1984)
303. V K Stankevich, L E Belozerov, B F Kukharev, B A Trofimov *Nauka — Proizvodstvu* (1) 19 (2004)
304. B A Trofimov, V I Lavrov, L N Parshina, V N Alekankin, V K Stankevich, V I Grigorenko *Zh. Org. Khim.* **18** 528 (1982) [b]
305. B A Trofimov, O V Vysotskaya, L A Oparina, L N Parshina, N K Gusarova *Nauka — Proizvodstvu* (6) 16 (2003)
306. L T Stroganova, S A Bol'shakova, T N Tuzhilkova, S V Amosova, N I Ivanova, O A Tarasova, M L Al'pert *Khim.-Farm. Zh.* **24** (2) 143 (1990) [l]
307. A M Vasil'tsov, B A Trofimov, S V Amosova, V K Stankevich, I S Zhikharev, V V Kuzin *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* 127 (1982)
308. N K Gusarova, M G Voronkov, B A Trofimov *Sulfur Rep.* **9** 95 (1989)
309. N A Chernysheva, N K Gusarova, B A Trofimov *Zh. Org. Khim.* **36** 11 (2000) [b]
310. A I Mikhaleva, B A Trofimov, A N Vasil'ev, P M Alkhimenkov, I S Zhikharev, L I Sineva, N P Vasil'ev *Izv. Sib. Otd. Akad. Nauk, Ser. Khim. Nauk* 150 (1981)
311. A I Mikhaleva, A M Vasil'tsov, L N Sobenina, V K Stankevich, B A Trofimov *Nauka — Proizvodstvu* (6) 27 (2003)
312. B A Trofimov, L A Oparina, V I Lavrov, L N Parshina *Zh. Org. Khim.* **31** 647 (1995) [b]
313. US P. 6504064; *Chem. Abstr.* **136** 69592 (2002)
314. B A Trofimov, L N Parshina, L A Oparina *Nauka — Proizvodstvu* (6) 2 (2003)
315. Russ. P. 1832674; *Byull. Izobret.* (6) (1995)
316. Russ. P. 1536761; *Byull. Izobret.* (21) (1994)
317. A I Mikhaleva, A M Vasil'tsov, L N Sobenina, V K Stankevich, B A Trofimov *Tekh. Mashinostr. Khim.* (4) 42 (2004)
318. Russ. P. 2059597; *Byull. Izobret.* (13) (1996)
319. A I Mikhaleva, A M Vasil'tsov, L N Sobenina, V K Stankevich, B A Trofimov *Nauka — Proizvodstvu* (6) 28 (2003)
320. A I Mikhaleva, A M Vasil'tsov, L N Sobenina, V K Stankevich, B A Trofimov *Nauka — Proizvodstvu* (6) 18 (2003)
321. V I Lavrov, L A Oparina, L N Parshina, V V Vins, B A Trofimov *Zh. Prikl. Khim.* 835 (1990) [e]
322. M Son, Q Shi, G Huang, Y Liang, Y Ma *Synthesis* 2482 (2005)
323. Z-J Han, R Wang, Y-F Zhou, L Liu *Eur. J. Org. Chem.* 934 (2005)
324. Y-F Kang, L Lie, R Wang, Y-F Zhou, W-J Yan *Adv. Synth. Catal.* **347** 393 (2005)
325. M Yamashita, K Yamada, K Tomioka *Adv. Synth. Catal.* **347** 1649 (2005)
326. M Ni, R Wang, Z-J Ban, B Mao, C-S Da, L Lie, C Chen *Adv. Synth. Catal.* **347** 1656 (2005)
327. P G Cozzi, J Rudolph, C Bolm, P-O Norrby, C Tomasini *J. Org. Chem.* **70** 5733 (2005)
328. S Xue, Q-F Zhou, L-Z Li, Q-X Guo *Synlett* 2990 (2005)
329. T Weil, P R Schreiner *Eur. J. Org. Chem.* 2213 (2005)
330. S Guillarme, K Plé, A Banchet, A Liard, A Haudrechy *Chem. Rev.* **106** 2355 (2006)
331. A Heutling, R Severin, S Doye *Synthesis* 1200 (2005)
332. A Heutling, F Pohlki, I Bytschkov, S Doye *Angew. Chem., Int. Ed.* **44** 2951 (2005)
333. T Shimade, G B Bajracharya, Y Yamamoto *Eur. J. Org. Chem.* 59 (2005)
334. J-S Herrmann, P W Roesky, S Blechert *Angew. Chem., Int. Ed.* **44** 7794 (2005)
335. K Marcsekova, B Wegener, S Doye *Eur. J. Org. Chem.* 4843 (2005)
336. A Tillack, V Khedkar, H Jiao, M Beller *Eur. J. Org. Chem.* 5001 (2005)
337. C Peppe, E S Lang, G N Ledesma, L B de Castro, O S D Barros, P de Azevedo Mello *Synlett* 3091 (2005)
338. R P Hsung, C A Zificsak, L-L Wei, C J Douglas, H Xiong, J A Mulder *Org. Lett.* **1** 1237 (1999)
339. L L Wei, J A Mulder, H Xiong, C A Zificsak, C J Douglas, R P Hsung *Tetrahedron* **57** 459 (2001)
340. I Fernandez, M I Monterde, J Plumet *Tetrahedron Lett.* **46** 6029 (2005)
341. I A Balova, V N Sorokoumov, S N Morozkina, O V Vinogradova, D W Knight, S F Vasilevsky *Eur. J. Org. Chem.* 882 (2005)
342. *Metal-Catalyzed Cross-Coupling Reactions* (Eds A de Meijere, F Diederich) (Weinheim: Wiley-VCH, 2004)
343. I A Maretina, B A Trofimov *Usp. Khim.* **75** 913 (2006) [*Russ. Chem. Rev.* **75** 825 (2006)]

344. S P McIlroy, E Clo, L Nikolajsen, P K Frederiksen, C B Nielsen, K V Mikkelsen, K V Gothelf, P R Ogilby *J. Org. Chem.* **70** 1134 (2005)
345. J W Y Lam, B Z Tang *Acc. Chem. Res.* **38** 745 (2005)
346. E H van Dijk, D J T Myles, M H van der Veen, J C Hummelen *Org. Lett.* **8** 2333 (2006)
347. K Li, Q Wang *Chem. Commun.* 4786 (2005)

[a] — *Petrol. Chem. (Engl. Transl.)*
[b] — *Russ. J. Org. Chem. (Engl. Transl.)*
[c] — *Russ. J. Gen. Chem. (Engl. Transl.)*
[d] — *Polym. Sci. (Engl. Transl.)*
[e] — *Russ. J. Appl. Chem. (Engl. Transl.)*
[f] — *Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*
[g] — *Chem. Heterocycl. Compd. (Engl. Transl.)*
[h] — *Dokl. Chem. (Engl. Transl.)*
[i] — *Mendeleev Chem. J. (Engl. Transl.)*
[j] — *J. Struct. Chem. (Engl. Transl.)*
[k] — *Russ. J. Organomet. Chem. (Engl. Transl.)*
[l] — *Pharm. Chem. J. (Engl. Transl.)*