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Methods for the synthesis of O-, S- and N-vinyl derivatives

Maria S. Ledovskaya, Vladimir V. Voronin, Konstantin S. Rodygin

Saint Petersburg State University
Universitetskaya nab., 7 – 9, 199034 St-Petersburg, Russian Federation

The currently known methods for the preparation of vinyl ethers, vinyl sulfides and enamines are analyzed and described systematically. The published data on the reactions of alcohols, thiols and various nitrogen-containing compounds with acetylene, resulting in the corresponding vinyl derivatives, are considered. The attention is focused on the application of convenient acetylene sources. Other modern approaches to the synthesis of vinyl derivatives are described in detail, including vinyl exchange and metathesis reactions, various types of cross-coupling and cleavage of organic compounds. Some specific synthetic routes to vinyl ethers, vinyl sulfides and enamines are presented in the last Section.
The bibliography includes 262 references.

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1. Introduction

Vinyl ethers and their nitrogen and sulfur analogues are widely used in organic synthesis, both in laboratory practice and in industry. The industrial applications of polymers and copolymers based on these compounds as adhesives, varnishes, paints and packing materials for food products, coatings and fillers for tablets are actively being developed.[1 – 14]

Despite the fact that the chemistry of vinyl ethers, their sulfur analogues and enamines has been comprehensively studied, it is still in progress. The number of publications dedicated to the use of vinyl derivatives in the synthesis of carbo- and heterocycles[2 – 7] and new biologically active molecules and natural compounds[8 – 10] increases constantly. Strategies for the synthesis of complex molecules with the use of vinyl derivatives in metathesis reactions are especially promising.[11 – 14] The interest in the application of these compounds in the synthesis of functionalized alkenes by cross-coupling has also increased in recent years.[15, 16] Therefore, the development of new methods for the preparation of vinyl derivatives (vinyl ethers, vinyl sulfides and enamines) and improvement of the existing strategies appears to be an interesting and relevant task.

The purpose of the present review is to systematically arrange and analyze the data, both reported in scientific literature and obtained by the authors, on the synthesis of vinyl ethers, their sulfur analogues (vinyl sulfides) and unsubstituted enamines (vinylamines) and to elucidate the general features of the preparation of these compounds.

The following chemical transformations underly the synthesis of vinyl derivatives:

— addition of alcohols, thiols and amines (or nitrogen heterocycles) to acetylene (pathway *a* in Scheme 1);
— vinyl exchange reactions (pathway *b*);
— metathesis reactions (pathway *c*);
— cross-coupling reactions (pathway *d*);
— various elimination reactions (pathway *e*);
— reactions involving organometallic compounds (pathway *f*).

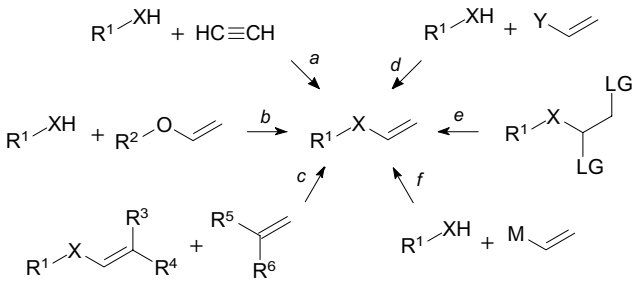
The material of the review is classified according to these types of reactions, with the approaches to the synthesis of vinyl ethers and their thio analogues and enamines being considered together. Particular attention is given to new studies, performed in the last 10 – 15 years, in this area of organic synthesis. A separate section (Miscellaneous methods) considers specific or rarely used synthetic pathways to vinyl derivatives.

M.S.Ledovskaya. PhD, Research Engineer at the Laboratory of Cluster Catalysis, Institute of Chemistry, SPbU.
Telephone: +7(812) 363 – 6592, e-mail: maria.s.ledovskaya@gmail.com
V.V.Voronin. PhD, Research Engineer at the same Laboratory.
E-mail: volgo-vv@mail.ru
K.S.Rodygin. PhD, Researcher at the same Laboratory.
E-mail: konstantinrs@rambler.ru
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Scheme 1



R^1, R^3, R^4, R^5, R^6 = Alk, Ar; R^2 = Alk, C(O)Alk; X = O, S, NH, NAlk, NAr; Y = Hal, $SnAlk_3$; LG = H, Hal, O_2CAlk, $SiAlk_3$, *etc.*; M = Li, HgOAc; LG is leaving group

2. Addition of alcohols, thiols and amines to acetylene

The addition of alcohols to acetylenes was discovered by A.E.Favorskii (cited from Ref. 17). While investigating isomerization of substituted acetylenes on heating with alcohol solutions of alkali, he demonstrated that alcohols react with substituted acetylenes to give vinyl ethers. Later, a method for the preparation of vinyl ethers by vinylation of alcohols with acetylene has been developed on the basis of this reaction.[18,19] In the literature, this method is often called the Favorskii–Shostakovskii reaction[20] or is associated with the German chemist Reppe,[21,22] who investigated a similar vinylation strategy.

Since the mid-20th century, the alcohol vinylation with acetylene is the key method for the synthesis of vinyl ethers. In industry, this reaction is usually carried out in autoclaves at elevated pressures and temperatures and in the presence of alkaline catalysts. Apart from aliphatic alcohols, this reaction can be extended rather easily to their aromatic analogues (phenols, naphthols, *etc.*), thiols, some amines and other compounds with X–H bond, where X = O, S, NAlk, NAr.[18–20,23] Below we successively consider most of the currently known vinylation reactions that involve unsubstituted acetylene; reactions of acetylene with alcohols, thiols and compounds with NH or NH_2 groups are discussed separately. A special group of general metal-catalyzed transformations of this type was highlighted in detail previously.[24,25]

The vinylation of alcohols, phenols and other hydroxyl-containing compounds can be depicted as the following general equation (Scheme 2).

Scheme 2



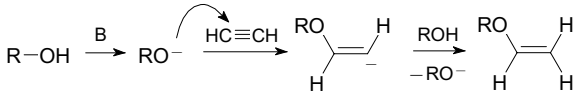
B is base

These reactions are usually catalyzed by strong bases. In an early study in this area,[26] it has been shown that different bases are required for the vinylation of different starting materials, since the rate of alcohol vinylation decreases in the series primary > secondary > tertiary. The vinylation of primary alcohols is usually performed, in the presence of alkalis, whereas the synthesis of vinyl derivatives of secondary or tertiary alcohols requires the presence of potassium alkoxides.[17,19–21,23] In addition, the use of alkalis for the synthesis of vinyl ethers of secondary or tertiary alcohols leads to the tar formation.[17]

The vinylation of aromatic alcohols (phenols, naphthols, *etc.*) requires more drastic conditions: it is necessary to use a larger amount of alkali, addition of water and higher temperature than in the case of aliphatic alcohols.[17,27] Water prevents polymerization of the vinyl ethers being formed and promotes the formation of aryloxide ions, *i.e.*, it increases the vinylation rate.[27–30]

Several groups of synthetic chemists[28–30] have simultaneously studied the addition of alcohols to acetylene or phenylacetylene and have shown that these reactions can be classified as nucleophilic addition. The mechanism of this transformation is shown in Scheme 3.

Scheme 3



An additional piece of evidence indicating that the formation of vinyl ethers occurs exactly by this mechanism is provided by the fact that the reaction is considerably accelerated when catalyzed by the potassium n-butoxide–18-crown-6 system.[31] The authors also reported the possibility to lower the reaction temperature by a factor of two, from 147 to 70 °C, by the addition of the crown ether. In the presence 18-crown-6, the amount of free alkoxide anions capable of catalyzing the reaction is higher than in the absence of the crown ether, which binds potassium ions.

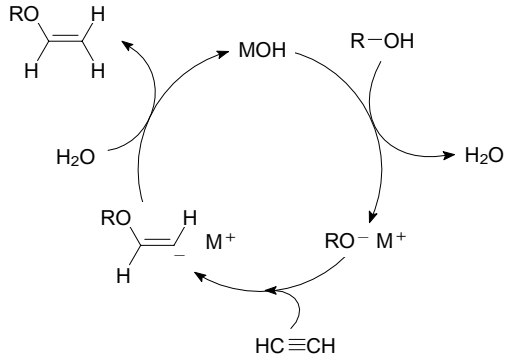
The conversion alcohol → vinyl ether can also be considered as a concerted process in which the acetylene molecule is attacked simultaneously by the anion formed upon proton elimination from the alcohol and by ROH.[20] However, in the case of unsubstituted vinyl ethers, *i.e.*, those containing a $CH{=}CH_2$ group, this issue is not of key importance.

The addition of alcohols to acetylene can be accompanied by a number of side reactions:[17,20] polymerization of acetylene,[32] formation of acid salts and some other reactions decreasing the efficiency of vinylation.[33–35] The KOH–dimethyl sulfoxide and KOH–hexamethylphosphoric triamide (HMPA) mixtures were stated as the best catalytic systems for the synthesis of vinyl ethers.[34] By using these mixtures, it is possible to achieve vinylation of lower primary alcohols in high yields. The vinylation of secondary alcohols also proved to be possible; however, the yield of vinyl ethers was moderate, which is attributable to lower reactivity of secondary alcohols in nucleophilic addition reactions. This procedure is safe, because the reactions are carried out under atmospheric pressure, and is rather simple: no by-products are formed, which considerably facilitates the isolation and purification of the vinyl ethers.[34] Later, the procedure of vinylation with acetylene in the presence of the superbasic KOH–DMSO catalytic system was successfully extended to phenols and naphthols: aryl vinyl ethers were prepared by this method in up to 74% yields.[36]

The vinylation of alcohols with acetylene was studied by quantum chemical calculations, which demonstrated that in the MOH–DMSO type systems (M = Na, K), the complexes $NaOH \cdot 4\,DMSO \cdot n\,H_2O$ or $KOH \cdot 5\,DMSO \cdot n\,H_2O$

(n = 1, 2) can be formed. In these complexes, water molecules act as the source of protons in the final stage, *i.e.*, they react with the carbanionic centre (Scheme 4).[37]

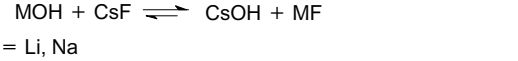
Scheme 4



R = Alk, Ar; M = Na, K

When present in excess, water can also have an adverse effect on the course of the reaction by suppressing dissociation of the initial alcohol.[37] In the presence of excess water, a number of side processes can take place with the participation of the catalyst and the starting reactants.[32–35] Apart from sodium and potassium hydroxides, the hydroxides of other alkali metals, for example, caesium, rubidium or lithium can be used for the catalytic vinylation of alcohols.[35, 38, 39] The following series of catalytic activity of alkali metal hydroxides was elucidated: $CsOH \cdot H_2O$ > $RbOH \cdot H_2O$ > $2\,KOH \cdot H_2O$ > NaOH > LiOH.[38] Caesium hydroxide has the highest catalytic activity. In some cases, hydrates were used in the reaction; therefore, side products were formed upon reactions of water with the starting compounds and acetylene, which had an adverse effect on the yield of vinyl ethers.[35, 38] Therefore, to avoid the side processes, a catalytic system was developed that minimized the amount of water in the reaction system. Caesium hydroxide hydrate was replaced by a mixture of caesium fluoride and anhydrous lithium or sodium hydroxide.[39] It is noteworthy that the reaction can be carried out by a solvent-free procedure. Presumably,[39] in this case, active and, what is most important, anhydrous caesium hydroxide is formed *in situ* during a simple exchange reaction (Scheme 5).

Scheme 5



M = Li, Na

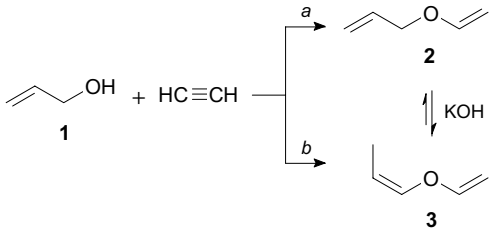
The best results were obtained using an NaOH – CsF mixture.[39] This can be attributed to higher solubility of sodium hydroxide in alcohol as compared with lithium hydroxide (this refers to the solvent-free procedure). The developed procedure was used to synthesize vinyl derivatives of primary and secondary aliphatic alcohols in moderate (secondary alcohols) to high (primary alcohols) yields. On going from the solvent-free procedure to the use of dimethyl sulfoxide as the solvent, the yields of vinyl ethers increased. In this case, like in the previous one,[34] the reactions were carried out at the ambient pressure. With the CsF – MOH – DMSO system, vinylation of non-reactive *tert*-butyl alcohol was even accomplihed (8% yield).[39]

Thus, the vinylation of primary and secondary aliphatic alcohols with unsubstituted acetylene requires a basic catalyst and heating of the reaction mixture. The reaction can be performed both in a closed system and in a flow reactor.[35] For better performance of the basic catalyst, it can be combined with dimethyl sulfoxide. In this case, the active complexes $NaOH \cdot 4\,DMSO \cdot n\,H_2O$ or $KOH \cdot 5\,DMSO \cdot n\,H_2O$ are generated *in situ*.[37] Apparently, complexes of the same type can also arise with other alkali metal hydroxides. A base is often defined as the reaction catalyst,[33–39] because it is taken in a small amount (5 mol.% to 20 mol.%). Moreover, the reaction does not proceed without a base, as no active alkoxide anion is generated.

The vinylation of aromatic alcohols can be accomplished using a similar strategy; however, it should be borne in mind that these substrates are less reactive towards nucleophilic addition to acetylene. The vinylation of phenols and naphthols requires higher amount of a base than that for the vinylation of aliphatic alcohols as well as addition of water or pressure rise in the reaction vessel.[36]

A specific feature of vinylation of allyl alcohol (**1**) is the possibility to control the composition of the product through the base: in the presence of a NaOH – NaOAc mixture, allyl vinyl ether (**2**) is predominantly formed, while on going to KOH, the reaction gives isomeric vinyl (*Z*)-propenyl ether (**3**).[40] Both compounds are valuable substrates for the synthesis of polymeric materials. In the presence of excess potassium hydroxide, allyl derivative **2** was found to be converted to isomer **3**.[40] When the concentration of KOH is decreased or it is replaced by a weaker base, the amount of the isomerization product in the reaction mixture decreases (Scheme 6).

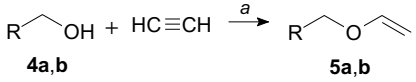
Scheme 6



(*a*) NaOH, NaOAc, DMSO, 80 °C, 12 atm, 4 h (82% yield);
(*b*) KOH, DMSO, 90 °C, 3 h (88% yield)

Vinyl ethers containing furan moieties are useful starting compounds for the preparation of polymers. The products of their polymerization or copolymerization can be used in pharmaceutical industry[23, 41] and for modification of lithium ion battery electrolytes.[23, 42] Good results were attained in the synthesis of these monomers from 2-(hydroxymethyl)furan (**4a**) and its saturated analogue **4b**: vinyl ethers **5a**,**b** were obtained in high yield in the presence of the KOH – DMSO system (Scheme 7).[43]

Scheme 7

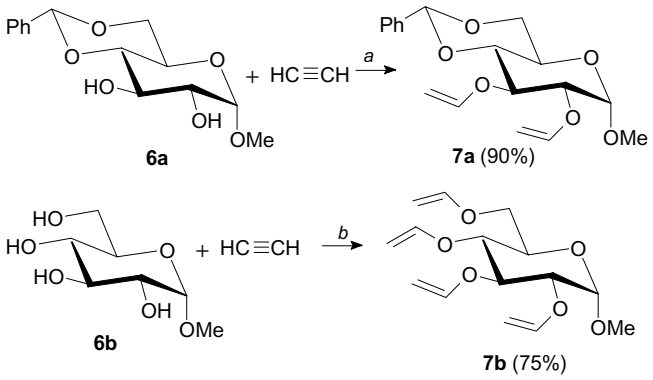


(*a*) KOH, DMSO; R = 2-Fu (**a**, 88% yield), tetrahydrofuran-2-yl (**b**, 91%); Fu is furyl

The preparation of vinylated derivatives of various natural compounds, for example, sugars, is of particular interest for chemists. These substrates are very promising due to the presence of chiral centres, the potential solubility in water and the ability to polymerize.

Relatively recently, carbohydrates **6a**,**b** have been converted to vinyl derivatives of glucose **7a**,**b** (Scheme 8).[44, 45] The product yields reached 90%. Successful vinylation of cellulose has also been reported.[46]

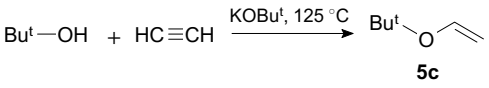
Scheme 8



(*a*) KOBu^t, DMSO, 113–117 °C, 15 h;
(*b*) KOH, DMSO, MeOH, 85–87 °C, 0.75 h

The synthesis of vinylated tertiary alcohols requires specific conditions. The proton elimination from the bulky tertiary alcohol molecule occurs with much more difficulty than that from primary or secondary alcohols. Several cases of addressing this problem have been reported. For instance, *tert*-butyl vinyl ether (**5c**) has been synthesized (Scheme 9).[47] Potassium *tert*-butoxide generated directly in the reaction vessel from potassium metal and *tert*-butyl alcohol was used as the base. The product yield was ~50%.

Scheme 9

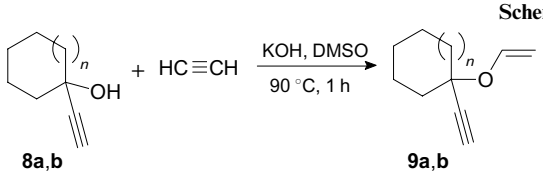


5c

Subsequently, this procedure was further developed and extended to a wider range of alcohols and acetylenes. *tert*-Butyl vinyl ether (**5c**) was prepared by the modified procedure in 75% yield.[48] The vinylation of the tertiary propargyl alcohols **8a**,**b** giving ethers **9a**,**b** in up to 40% yields has been reported (Scheme 10).[49]

There are few publications devoted to the synthesis of thio analogues of vinyl ethers, although these structures could be useful in organic synthesis, as they have a reactive multiple bond in their molecules. The simplest method for

Scheme 10

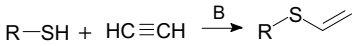


8a,**b** **9a**,**b**

n = 1 (**a**), 2 (**b**)

the preparation of vinyl thioethers (vinyl sulfides) is based on the nucleophilic addition of thiols to acetylene. Regarding the reaction mechanism, this addition is similar to vinylation of alcohols with acetylene. Generally, it can be represented by the reaction equation depicted in Scheme 11.

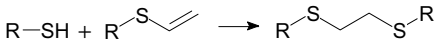
Scheme 11



It is noteworthy that this reaction with symmetrical or unsymmetrical alkynes can be carried out for thiols as well as for selenium and tellurium derivatives,[50] but only in the presence of metal-containing catalysts. Possible catalysts are gold[51] or palladium[52–55] complexes. A key feature of catalytic transformations of this type is high stereo- and regioselectivity. These reactions afford substituted vinyl derivatives.

Since sulfur is a better nucleophile than oxygen, the addition of the thiol molecule to vinyl sulfide can occur as a side reaction (Scheme 12).

Scheme 12

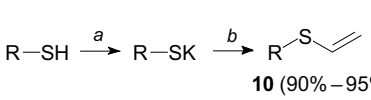


R = Alk, Ar

In order to suppress this reaction, it was proposed to carry out vinylation in the presence of a large excess of acetylene.[56, 57] In general, the synthesis of alkyl vinyl sulfides *via* the reaction of thiols with acetylene is similar to the synthesis of vinyl ethers. However, the vinylation of thiols should be conducted under milder conditions. Heating above 100 °C leads to resinification of vinyl sulfides; therefore, the reaction is carried out at lower temperature.[58] For increasing the acetylene concentration in the reaction medium (and suppressing side processes), it is necessary to use the solvents that dissolves acetylene well. Shostakovskii *et al.*[58] selected the following optimal conditions for the preparation of alkyl vinyl sulfides: 70–90 °C, dioxane as the solvent and elevated pressure (up to 30 atm). The yields of vinyl thioethers were 60%–76% in this case.

Later, this procedure was modified. In particular, vinylation of thiols was conducted in aqueous alkali using a large excess of alkali metal (usually potassium) hydroxide.[59, 60] In this case, the corresponding potassium thiolate rather than thiol participates in the reaction (Scheme 13). This method implies a high excess of acetylene and elevated pressure. This procedure was used to prepare unsubstituted aliphatic vinyl sulfides **10** and phenyl vinyl sulfide (**10a**). Apparently, this procedure can also be used to obtain other vinyl thioethers, with the reaction conditions being adjusted taking into account the structural features of the starting thiols.

Scheme 13

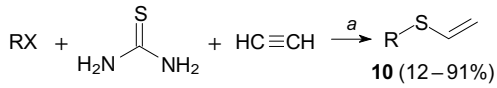


10 (90%–95%)

(*a*) KOH, H_2O, 20–24 °C, 1 h; (*b*) HC≡CH, H_2O, 100–120 °C, 3–5 h; R = Alk (5 examples), Ph

Another approach to the synthesis of vinyl thioethers **10** is based on the reaction of alkyl or aryl halides with thiourea and acetylene in alkaline medium (Scheme 14).[61, 62]

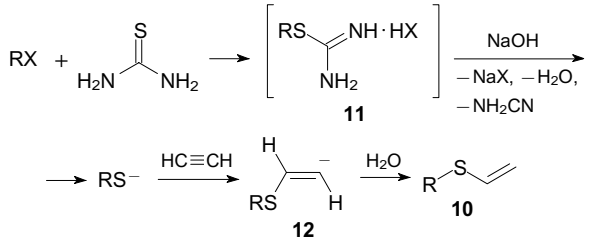
Scheme 14



(*a*) NaOH, H_2O, Δ; R = Alk (7 examples), Ar (3 examples), CH_2═$CHS(CH_2)_4$, $Et_2N(CH_2)_2$, $Me_2N(CH_2)_2$, tetrahydrofuran-2-ylmethyl, tetrahydrothiophen-2-ylmethyl; X = Hal

The mechanism of this transformation includes the *in situ* formation of isothiouronium salt **11**, which is then cleaved under the action of a base to give the thiolate anion and cyanamide. Then the reactive thiolate ion attacks acetylene to give carbanion **12**, which reacts with a source of proton (water) to afford vinyl thioether (Scheme 15).[61]

Scheme 15



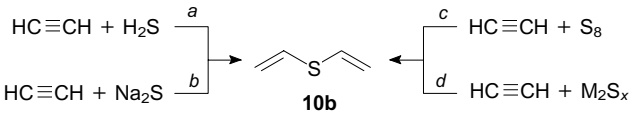
A variety of alkyl vinyl thioethers and a number of their derivatives with functional groups have been synthesized using this strategy, including aminoalkyl vinyl sulfides valuable for synthetic organic chemistry.[62]

A special example of vinyl ether is divinyl sulfide **10b**. Several approaches to its synthesis have been reported.[63 – 65] Currently, four methods involving the use of acetylene are known.

All these methods are based on the reaction of an active sulfur-containing anion either introduced or generated *in situ*. When hydrogen sulfide is used for the synthesis of divinyl sulfide (pathway *a* in Scheme 16),[64, 65] the reactive hydrosulfide anion is generated from H_2S. Sodium sulfide (pathway *b*) reacts by a similar route. In the presence of sulfur, the reaction involves ions of the $^-S_8-OH$ structure (pathway *c*). In the case of alkali metal polysulfides (pathway *d*), the reaction is likely to follow a similar mechanism.

The preparation of vinylated nitrogen compounds is an important task of synthetic organic chemistry, as polymeric materials based on them are demanded in various branches of industry.[1, 66, 67] The synthesis of N-vinylated nitrogen heterocycles is of most interest for synthetic chemists. For example, *N*-vinylpyrrole or *N*-vinylindole polymers possess a number of useful properties: polyvinylpyrrolidone is used in pharmaceutical industry as a drug filler or coating component,[67] while polyvinylindoles have a unique set of physical properties, which makes them suitable for the manufacture of semiconductor materials and electroluminescent displays.[66]

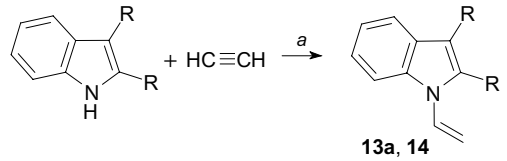
Scheme 16



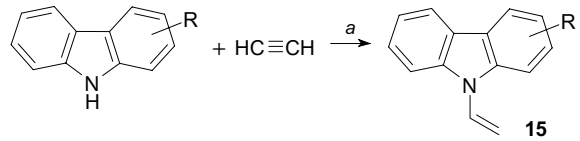
(*a*) MOH, DMSO (98% yield); (*b*) NaOH, DMSO, H_2O (80% yield); (*c*) KOH, DMSO, H_2O, 80 – 120 °C, 12 atm (80% yield); (*d*) KOH, DMSO, H_2O (70% – 90% yields); M = Na, K; *x* = 2 – 4

The history of vinylation at the nitrogen atom is associated with the name of Reppe,[68] a German chemist who was the first to synthesize vinyl derivatives of indole, carbazole and some their derivatives by reactions with acetylene. The vinylation procedure was generally similar to the procedure used to prepare vinyl ethers (Scheme 17; Δ stands for heating, *P* is high pressure): the heterocycle and acetylene are heated in a closed vessel at an elevated pressure in the presence of a catalytic amount of potassium hydroxide in an appropriate solvent. The solvents used are cycloalkanes or ethylene glycol. Vinyl derivatives of indole (**13a**), tetrahydrocarbazole (**14**) and carbazoles (**15**) were obtained in up to 90% yields.

Scheme 17



(*a*) KOH, Δ, *P*; R = H (**13a**); R – R = $(CH_2)_4$ (**14**)

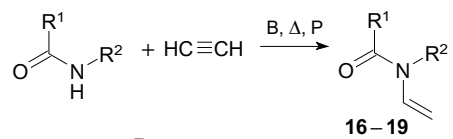


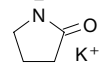
(*a*) KOH, Δ, *P*; R = H, Pr^i (in different positions)

This procedure was later modified and improved: it was proposed to replace the solvent by dioxane,[69] and the yield of *N*-vinylindole (**13a**) was thus increased to 94%.[70] The vinylation was catalyzed by the KOH – DMSO superbasic system.

In 1943, a procedure was developed for the synthesis of N-vinylated lactams, including widely used *N*-vinylpyrrolidone (*N*-vinylpyrrolidin-2-one, **16**).[71] It was also based on the reaction of the appropriate nitrogen compound with acetylene in the presence of a base at an elevated pressure and high temperature (100 – 150 °C) (Scheme 18).

Scheme 18



B = K, KOEt,  ; R^1-R^2 = $(CH_2)_3$ (**16**), $(CH_2)_5$ (**17**),

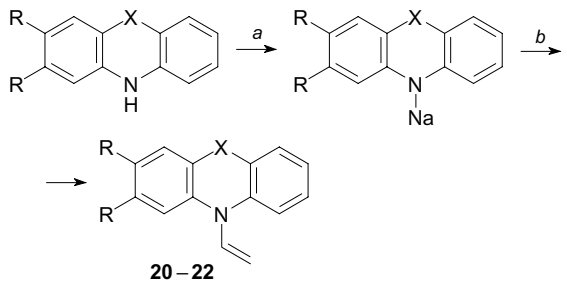
 (**18**); R^1 = Me, R^2 = Ph (**19**)

Vinylated lactams **17** and **18** and acyclic *N*-vinyl-*N*-phenylacetamide (**19**) were prepared in good yields using this strategy.[71] The vinylation of cyclic derivatives was

conducted in the presence of the pyrrolidone potassium salt, while in the case of *N*-phenylacetamide, potassium ethoxide was used. If potassium metal was used, the base was apparently formed *in situ* in the reaction between the lactam and potassium. Subsequently, various alkyl-substituted *N*-vinylindoles **13** were prepared by a similar procedure in the presence of an alkali metal for the *in situ* generation of a base from the substrate being vinylated.[72]

An example of vinylation of diarylamines with sodium hydride as the base has been reported.[73] The reaction of the initial compounds with NaH gives rise to reactive bases — the corresponding sodium derivatives, which react with acetylene to give *N*-vinylamines **20**–**22** (Scheme 19). A benefit of this method is the possibility to conduct the reaction at an atmospheric pressure of acetylene. The procedure seems unsafe, because the amine may react with sodium hydride with hydrogen evolution.

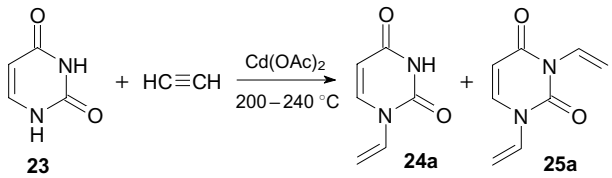
Scheme 19



(*a*) NaH, THF, N_2; (*b*) HC≡CH, DMAC, 140–150 °C; R–R is benzo, X is absent (**20**); R = H: X = $(CH_2)_2$ (**21**), CH=CH (**22**); DMAC is *N*,*N*-dimethylacetamide

The alkaline reagents applied for the synthesis of vinylpyrroles, vinyldiarylamines and so on are inapplicable as catalysts for uracil (**23**) vinylation with acetylene. Therefore, weakly basic cadmium acetate was proposed for this purpose (Scheme 20).[74] This reaction gives mono- (**24a**) and divinylated (**25a**) uracil, with their total yield reaching 43%.

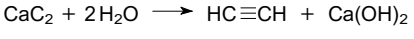
Scheme 20



On the one hand, the synthesis of vinyl ethers, vinyl sulfides and enamines by the addition of alcohols, thiols and amines to acetylene is relatively simple from the chemical standpoint and does not require expensive starting materials, because the cost of acetylene and the other organic reactants is rather low. One more benefit of these methods is the applicability of readily accessible inorganic bases as catalysts. On the other hand, handling of acetylene gas requires extra caution, as it is explosive.[21] Furthermore, gas metering can require special equipment. Therefore, synthetic chemists are in permanent search for an acetylene substitute that would be safe and convenient to handle.

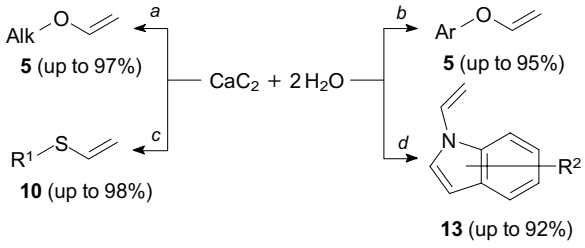
An increasing number of recent publications have been devoted to the use of calcium carbide as the source of acetylene in organic synthesis.[75] Calcium carbide is a solid that reacts with water to give acetylene gas (Scheme 21).

Scheme 21



The replacement of acetylene fed from a cylinder by solid CaC_2 makes possible the precise calculation of the gaseous reactant amount, and considerably lower the cost of equipment, because a gas metering device is no longer needed. Calcium carbide has been used to vinylate a wide range of compounds (Scheme 22), including numerous primary and secondary alcohols (in particular, natural ones: polyols, steroids),[76,77] phenols and naphthols,[76–78] aliphatic and aromatic thiols [79,80] and indoles.[78]

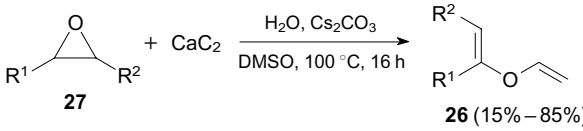
Scheme 22



(*a*) AlkOH, B, DMSO, Δ; (*b*) ArOH, B, DMSO, Δ; (*c*) R^1SH, KOH, DMF, 100 °C, 3 h; (*d*) R^2-substituted indole, Cs_2CO_3, DMSO, 100 °C, 12 h; Alk is a primary or secondary alkyl group; Ar = Ph, Naph and substituted analogues; R^1 = Ar, Het, ArNH, Alk (15 examples); R^2 = H, Alk, Hal (in different positions), 3-CHO, 5-NO_2, 5-OMe, 5-NH_2; B = KOH/KF, Cs_2CO_3; Naph is naphthyl

An unusual example of the synthesis of vinyl ethers **26** from oxiranes **27** is given in a recent publication[81] (Scheme 23). The products seem useful for the synthesis of cross-linked polymers.

Scheme 23

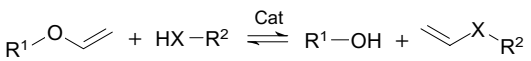


R^1 = Ar, Het; R^2 = H, Ph

3. Vinyl exchange reactions

The vinyl exchange implies migration of the vinyl group from one compound to another. Thus it is possible to convert easily accessible vinyl derivatives to more complex molecules. This reaction is depicted in general form in Scheme 24.

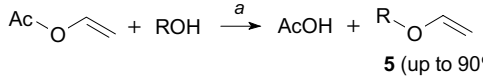
Scheme 24



R^1 = Alk, Acyl; R^2 = Alk, Ar, Alkenyl, *etc.*, X = O, S, NH, NAlk, NAr; Cat is catalyst

This is an equilibrium reaction. For shifting the equilibrium (to obtain the desired vinyl derivative), a catalyst is usually required. Alkyl vinyl ethers or vinyl acetate serve as the vinyl donors. The first examples of vinyl exchange were concerned with the synthesis of vinyl carboxylates. For example, mixing of vinyl acetate or vinyl butyrate with formic acid in the presence of mercury oxide resulted in the formation of vinyl formate and acetic or butyric acid, respectively.[82] Later, it has been shown that mercury compounds can also catalyze the exchange reaction between vinyl acetate and various alcohols.[83] This strategy was used to prepare a series of vinylated primary alcohols **5** (Scheme 25), and it was shown that vinyl exchange reaction is applicable to the synthesis of secondary and tertiary vinyl ethers and ethers of functionalized alcohols.

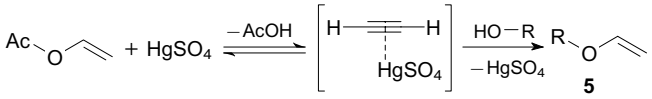
Scheme 25



(*a*) $Hg(OAc)_2$, H_2SO_4, from −30 to −14 °C; R = Et, Pr^i, Bu^n, Bu^t, MeO_2CCH_2, tetrahydrofuran-2-ylmethyl

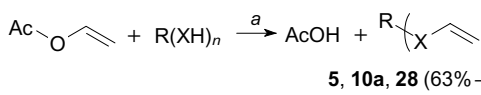
A mixture of mercury acetate and sulfuric acid was used as the catalyst; ready mercury sulfate is also suitable.[83] The reaction mechanism proposed by the authors is as follows: vinyl acetate reacts with mercury salts to give acetic acid and a reactive Hg acetylene complex (Scheme 26). The reaction of this complex with alcohol gives the corresponding vinyl ether **5** and mercury salt.

Scheme 26



Subsequently, this strategy was extended to a wider range of substrates: various primary,[84,85] secondary and tertiary alcohols[86,87] and phenols[88,89] were vinylated in this way. It was shown that mercury compounds can be replaced by iridium, rhodium, platinum or ruthenium complexes.[90] When the reaction is catalyzed by bis(cycloocta-1,5-diene)diiridium(I) dichloride ($[Ir(cod)Cl]_2$), vinyl derivatives of primary, secondary and tertiary alcohols (**5**) and diols (**28**) are formed in 63% – 100% yields, depending on the substrate structure. An example of phenyl vinyl sulfide (**10a**) synthesis in 92% yield has also been reported[90] (Scheme 27).

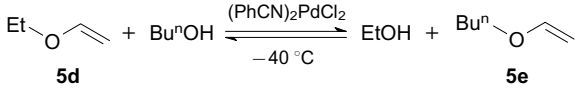
Scheme 27



(*a*) $[Ir(cod)Cl]_2$, Na_2CO_3, PhMe, argon, 100 °C; ROH = n-C_8H_{17}OH, BnOH, $Ph(CH_2)_2OH$, 1-AdOH, PhOH; $R(OH)_2$ = $HO(CH_2)_6OH$, adamantane-1,3-diol, hydroquinone; RSH = PhSH; Ad is adamantyl

Not only vinyl acetate, but also vinyl ethers can be used as vinyl group donors. The addition of n-butanol to ethyl vinyl ether (**5d**) in the presence of bis(benzonitrile)palladium(II) dichloride on cooling gives rise to an equilibrium mixture containing ethyl vinyl (**5d**) and n-butyl vinyl (**5e**) ethers, ethanol and n-butanol (Scheme 28).[91]

Scheme 28



It has been shown[92] that the equilibrium of this reaction can be shifted by replacing the catalyst by diacetato(2,2′-bipyridyl)palladium(II) or diacetato(1,10-phenanthroline)-palladium(II). By using these complexes, an excellent result was attained, namely, the yield of the target vinyl ether reached 93%. A number of vinyl ethers derived from primary, secondary and tertiary alcohols have been prepared by an analogous procedure. The product yields were 61% – 98%. Diacetato(4,7-diphenyl-1,10-phenanthroline)-palladium(II) and bis(trifluoroacetato)(4,7-diphenyl-1,10-phenanthroline)palladium(II) were used as catalysts. With the latter catalyst, allyl vinyl ethers were synthesized in high yields (80% – 96%).[93]

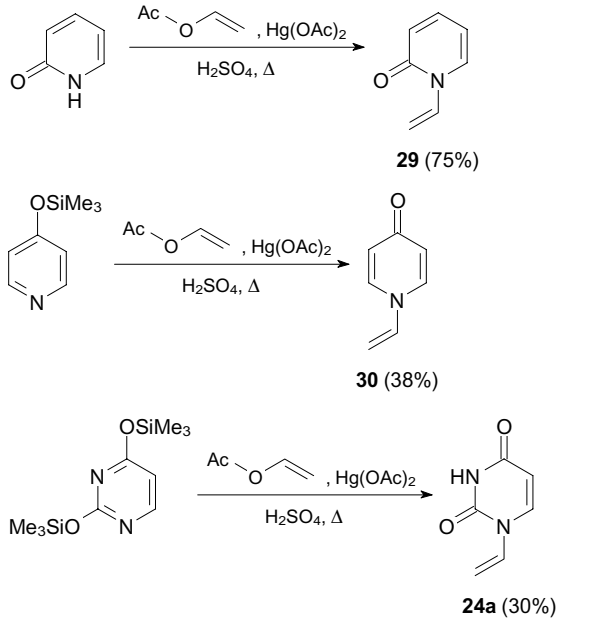
A similar procedure was used for the vinylation of monosaccharides and steroids in the presence of diacetato(4,7-diphenyl-1,10-phenanthroline)palladium(II).[94,95] Attempts have also been made to select another catalyst for the vinylation of alcohols; however, they have not been fully successful. Vinyl exchange in the presence of a gold-based catalyst has been reported. The $AuPPh_3Cl$ – AgOAc system was used to catalyze the synthesis of vinyl derivatives of primary, secondary and tertiary alcohols,[93–96] but the product yields were, on average, lower than in the preceding studies.

Enamines have been prepared by the vinyl exchange reactions similarly to vinyl ethers and their thio analogues. In general, vinyl acetate was used as the source of the vinyl group, and mercury, palladium and iridium compounds were employed as catalysts.[97–109] This approach was applied for the synthesis of uracil derivatives, which have been used in polymer chemistry.[97] As in the case of alcohol vinylation, a mixture of mercury acetate and sulfuric acid served as the catalyst, but since the vinyl exchange with nitrogenous bases occurs very slowly, the reaction mixture had to be heated.

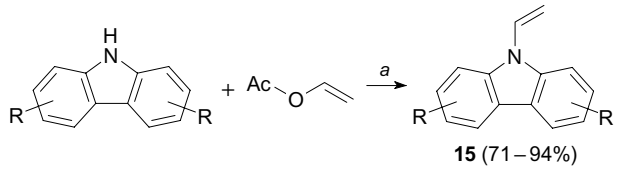
Vinyl exchange allows simultaneous vinylation at the nitrogen atom and removal of the trimethylsilyl protection of the substrate. Apart from compounds **24a**, **29** and **30** (Scheme 29), derivatves of cytosine,[97,98] thymine, adenine,[99] guanine,[100] imidazole[101,102] and triazole[103] were obtained in this way. The synthesis of vinylcarbazoles **15** by the vinyl exchange reaction has been reported.[104] Several catalysts have been tested, and the best results were obtained with bis(cycloocta-1,5-dienyl)diiridium(I) dichloride: the yields of products **15** were 71% – 94% (Scheme 30). *N*-Vinyl-2,3-dimethylindole was formed by this procedure in a yield of 60%.

N-Vinylpyrrolidone,[105] *N*-vinylphthalimide[106] and *N*(3)-benzoyl-*N*(1)-vinylthymine[107] can also be obtained, without the use of a mercury-containing catalyst, by the

Scheme 29



Scheme 30

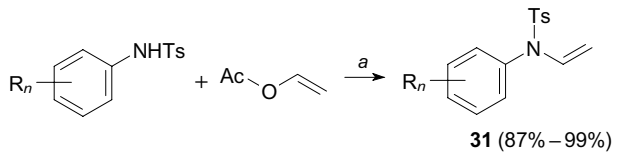


(*a*) $[Ir(cod)Cl]_2$, Na_2CO_3, PhMe, argon, 100 °C; 2 R = 2 H, 3,6-Bu^t_2, 3,6-Cl_2, 3,6-Br_2, 2,7-Br_2

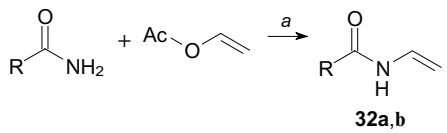
reaction of vinyl acetate with appropriate NH-substrates in the presence of sodium tetrachloropalladate(II) and potassium carbonate.

A method for the synthesis of N-vinylated sulfonamides and acylamides, which can also serve to vinylate the amide NH_2 function, has been reported.[108] This is still the only publication describing the vinylation of amides. Products **31** and **32a**,**b** were prepared by this procedure (Scheme 31).

Scheme 31



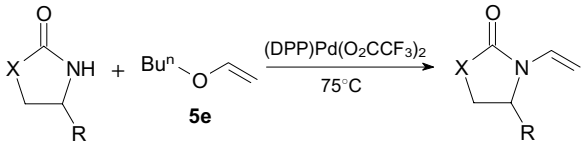
(*a*) $Pd(OAc)_2$, IPr, K_2CO_3, rt; R_n = H, 4-Me, 2,4-Me_2, 3-CF_3, 3-NO_2, 4-Ac, 4-OMe; Ts is *p*-toluenesulfonyl, IPr = 1,3-bis(2,4,6-triisopropylphenyl)imidazol-2-ylidene



(*a*) $Pd(OAc)_2$, IPr, K_2CO_3, rt; R = CH_2=CH (**a**, 37% yield), Ph (**b**, 36%)

Enamides, for example, *N*-vinylpyrrolidone (**16**) and oxazolones **33a**–**c**, which are widely used by synthetic chemists, can be prepared directly by the vinyl exchange reaction between n-butyl vinyl ether and appropriate amides (Scheme 32).[109] Apart from cyclic amides, trifluoroacetamide was vinylated by this method (76% yield). In the latter case, ethyl vinyl ether served as the source of the vinyl group. This strategy also underlies the synthesis of *N*-vinylsulfonamides.[109]

Scheme 32

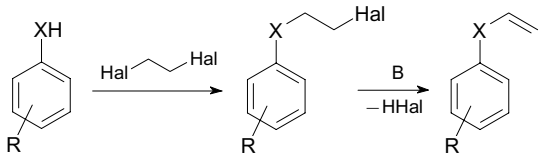


X = CH_2, R = H (**16**); X = O: R = H (**33a**), Pr^i (**33b**), Bn (**33c**); DPP is 4,7-diphenyl-1,10-phenanthroline

4. Elimination reactions for the synthesis of vinyl derivatives

Elimination implies splitting off of some group from the starting compound or intermediate. This process is often preceded by the addition reaction. Nevertheless, a particular transformation is classified as elimination on the basis of its last step. Elimination is one of the most popular methods for the synthesis of vinyl derivatives. A classical scheme for transformations of this type includes two steps: replacement of hydrogen atom at an oxygen, sulfur or nitrogen atom by some group (most often, haloalkyl) and subsequent direct elimination of the appropriate group in the presence of a strong base (Scheme 33).

Scheme 33

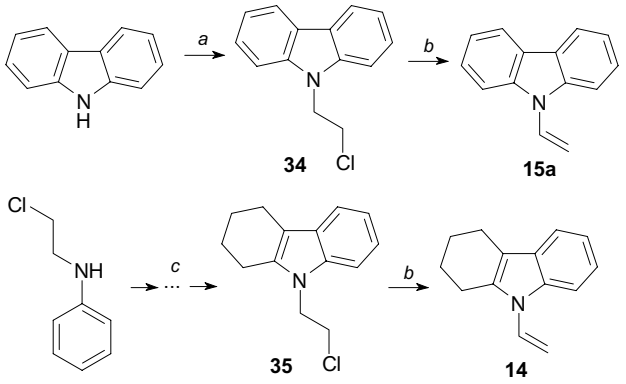


X = O, S, NH, NAlk, NAr; R = H, Alk, Hal, *etc.* (in different positions)

This method has proved to be useful for the synthesis of vinyl derivatives with diverse structures in test to preparative amounts. The key drawbacks of this method are a large number of steps and the lack of atom-economy. All kinds of substituents, bases, additives and catalysts have been tested throughout more than a hundred-year history of optimization of this method.

N-Vinylcarbazole (**15a**) and *N*-vinyltetrahydrocarbazole (**14**) were prepared from respective *N*-(2-chloroethyl)carbazoles **34** and **35** (Clemo–Perkin method) to study their reactions with acids (Scheme 34).[110]

Scheme 34

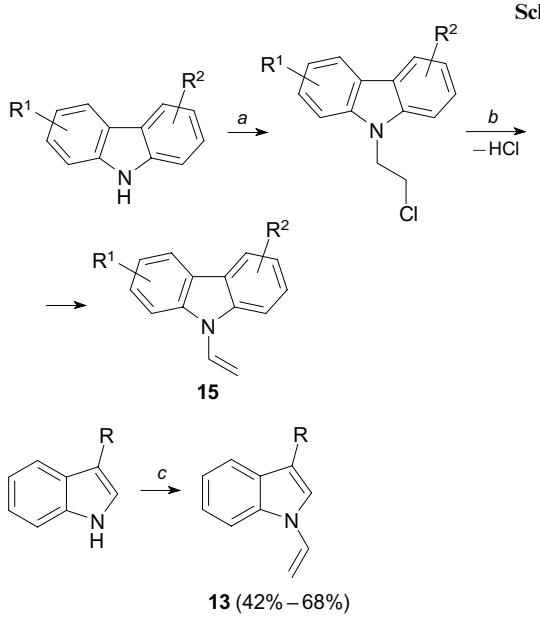


(*a*) $TsO(CH_2)_2Cl$, NaOH, Me_2CO; (*b*) KOMe, MeOH, Δ, 4 h; (*c*) 1) H^+, $NaNO_2$; 2) Zn-dust, AcOH, cyclohexanone, 65 °C

In the last step, a methanol solution of potassium methoxide was used as a base for hydrogen chloride elimination. Chloroethyl tetrahydrocarbazole derivative **35** was synthesized *via* the intermediate nitroso compound followed by hydrolysis. It is noteworthy that chloroethyl carbazole derivatives could not be obtained from the corresponding β-hydroxy derivatives; therefore, the synthetic strategy shown in Scheme 34 was chosen. Drawbacks of this method are a large amount of 2-chloroethyl tosylate needed for the synthesis and relatively long time needed for the procedure. Subsequently the method was modified [111] to prepare, for example, 3(6)-halo- and dihalogenated derivatives of vinylcarbazoles (up to 92% yields) meant for the subsequent polymerization.[112] An ethanol solution of KOH was used as a base in the last elimination step.

The employment of phase transfer catalysts makes it possible to rather easily prepare *N*-vinylcarbazoles **15** (Refs 113 and 114) and *N*-vinylindoles **13**.[115,116] Usually, these procedures include two steps (Scheme 35).[117–119] In the first step, the specified carbazole is haloethylated with 1,2-dichloroethane [119] or 1,2-dibromoethane [120] in the presence of a phase transfer catalyst, while the second step is base-mediated elimination of hydrogen halide under the action of a base. Ethylene gas and bromine [121] or sulfuryl chloride [122] can be used as haloethylating reagents for the synthesis of S-vinyl derivatives, for example, phenyl vinyl sulfide. Working with gases is rather difficult; furthermore, the authors noted bromine leakage from the reaction medium, which also complicated the synthesis. Either 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) or the traditional potassium hydroxide base is used in the elimination step. The purity of the obtained *N*-vinylindole (**13a**) and its methyl derivatives is sufficient for using them for radical polymerization involving chain transfer agents [66] or for asymmetric hydroformylation.[123]

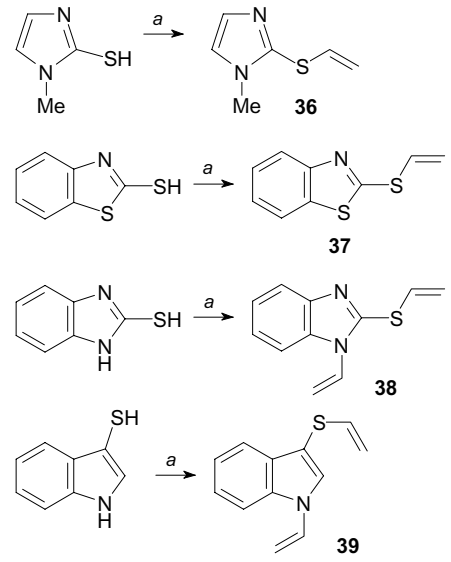
Scheme 35



(*a*) $Cl(CH_2)_2Cl$, TEBACl, NaOH, H_2O; (*b*) KOH; (*c*) $Cl(CH_2)_2Br$, KOH, 18-crown-6, PhMe; R^1, R^2 = H or Hal (in positions 1, 3, 6 and 8); R = H, CHO, Ac, C(Me)=NOH; TEBA is benzyltriethylammonium

Due to elimination of HCl from dichloroethane, vinyl chloride can be detected in the reaction mixture. After optimization of reaction conditions, the yield of the target products can reach 90%. Under the same conditions, thiols are converted to vinyl thioethers (*e.g.*, compounds **36** and **37**), while substrates containing two reaction centres form divinyl derivatives (*e.g.*, compounds **38** and **39**) [115] in up to 50% yields (Scheme 36). Unfortunately, this reaction is not selective, and either S- or N-vinylated products cannot be obtained separately.

Scheme 36



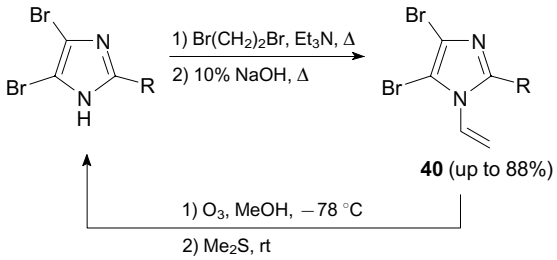
(*a*) $Cl(CH_2)_2Br$, KOH, 18-crown-6, PhMe

Instead of dichloroethane and KOH, it is possible to use dibromoethane or triethylamine [124] or *N*-chlorosuccinimide (NCS) and pyridine,[125] in particular, for the synthesis of *S*-vinyl sulfilimine.[126]

Imidazole dibromo derivatives also act as substrates, and the subsequent alkalification affords N-vinylated imidazoles **40** (Scheme 37).[124] They can give off the vinyl group to produce NH-imidazoles.

The vinyl substituent at the nitrogen atom in compounds **40** can be considered as a protecting group. Devinylation usually occurs with quantitative product yields.[127]

Scheme 37

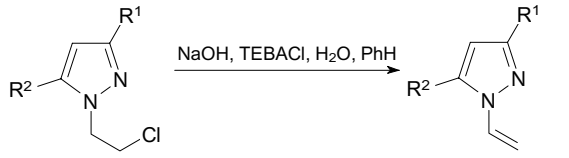


R = H, CH_2OH, CH(OH)Me, CHO, SMe, SPh

The major problems in this case are the condensation of acetaldehyde formed in the reaction and oxidation of the regenerated imidazoles. Under certain conditions, it is possible to avoid these processes; therefore, the vinyl group is obviously undervalued as the protection for NH, OH and SH groups in diversified substrates.

In the presence of a phase transfer catalyst (benzyltriethylammonium chloride), dehydrochlorination of *N*-(2-chloroethyl)pyrazoles also proceeds rather easily (Scheme 38).[128] In the absence of this catalyst, the yields of *N*-vinylpyrazoles **41** decrease to 10%, which is attributable, most likely, to an improperly chosen system of solvents, because similar dehydrochlorination of the same substrates proceeds even in water and gives products in high yields.[129] Phase transfer catalysts, for example, tetra-n-propylammonium bromide, can also be used in the synthesis of vinyl thioethers, which are formed in preparative yields (up to 73%).[130]

Scheme 38

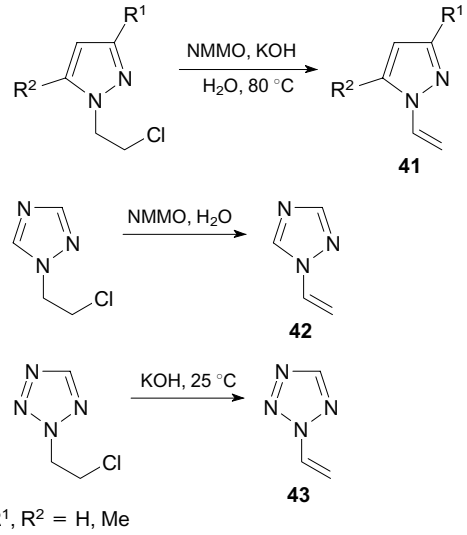


R^1, R^2 = H, Me

A fairly unusual phase transfer catalyst is triisopropylsilane, which is converted to the corresponding silanolate in the presence of a strong inorganic base (for example, KOH).[131] The silanolate formed *in situ* helps to synthesize alkenes even from primary alkyl halides without the formation of side ethers or alcohols.

In the case of *N*-(2-chloroethyl) derivatives of pyrazoles, triazole and tetrazole, the dehydrochlorination giving products **41**–**43**, respectively, can also occur in the absence of a phase transfer catalyst (Scheme 39). *N*-Methylmorpholine *N*-oxide (NMMO) as a mixture with KOH can be used as a soft base.[129] The process is facilitated with increasing number of nitrogen atoms in the heterocycle. Indeed, dehydrochlorination of *N*-(2-chloroethyl)pyrazoles requires heating of the reactants to 80 °C, while in the case of analogous tetrazole, the reaction already starts at room temperature. Seven examples of preparation of vinylated azoles in 75% to 80% yields have been reported.[129]

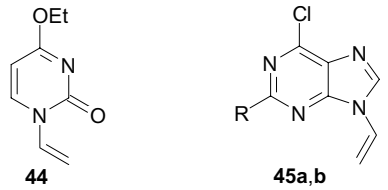
Scheme 39



R^1, R^2 = H, Me

For the synthesis of polymers based on nitrogenous bases, *N*-vinyl pyrimidines (**44**) and purines (**45a**,**b**) can be obtained in 55%–80% yields.[132]

Structures 44, 45

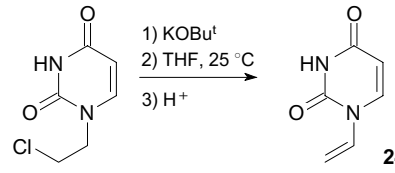


44 **45a**,**b**

R = H (**a**), Cl (**b**)

N-Vinyluracil (**24a**) is formed from the corresponding chloro derivative in the presence of $KOBu^t$ in DMSO[133] or in THF[134] at room temperature (Scheme 40). Other methods based on dehydrochlorination such as the reaction with potassium *tert*-butoxide in refluxing *tert*-butyl alcohol[135] or the reaction with alkali metals under the conditions of *N*-vinylpyrrolidone (**16**) synthesis[136] give compound **24a** in very low yields.

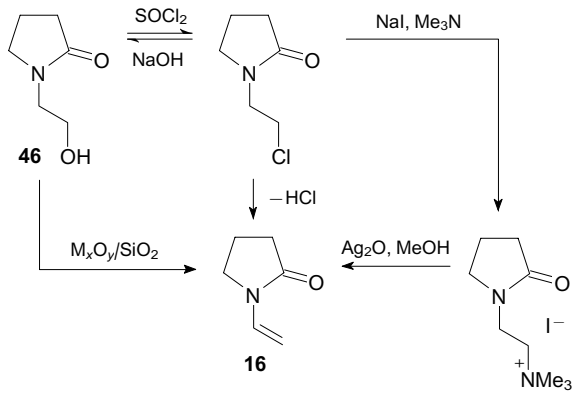
Scheme 40



One method for the synthesis of *N*-vinylpyrrolidone also includes the dehydrohalogenation step. The starting compounds used for this purpose are 2-aminoethanol and butyrolactone, which are successively passed above the dehydrating catalyst[137] on heating to 180–190 °C and are treated with thionyl chloride. Dehydrohalogenation of the chloroethyl derivative thus formed occurs in the presence of potassium hydroxide or sodium amide, the product yield being up to 76%.[136]

N-(2-Hydroxyethyl)pyrrolidone (**46**) is also a convenient starting compound for the preparation of *N*-vinylpyrrolidone (**16**).[138] A variety of metal oxides supported on silica gel have been tested as dehydrating agents for this substrate (Scheme 41).[139, 140]

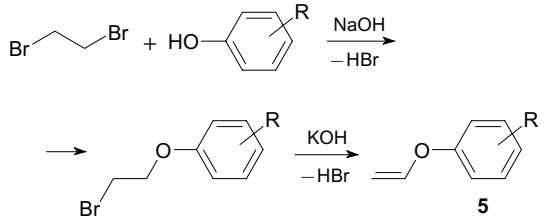
Scheme 41



M = Li, Na, K, Pb, Cs, Ca, Sr, Ba

For studying the acid hydrolysis of saturated ethers, a series of aryl vinyl ethers **5** were prepared by the classical two-step scheme (Scheme 42).[141] This method was initially proposed for the synthesis of α,β-unsaturated[142, 143] ethers and then modified.[144] By steam distillation followed by vacuum distillation of the resulting ethers, pure products can be isolated in large amounts. Alcohol mixtures with water or DMSO were used most often as solvents.[15]

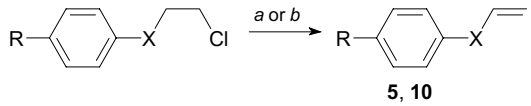
Scheme 42



R = Me, OMe, Cl (in different positions)

Instead of the EtOH – EtONa mixture (conditions *b* in Scheme 43), *tert*-butyl alcohol and potassium *tert*-butoxide (conditions *a*) proved to be more advantageous for the preparation of aryl vinyl ethers **5** and their thio analogues **10**. In the latter case, the products formed in 76% to quantitative yields, whereas in the former case, the yields of vinyl ethers **5** sharply decreased (14% – 28% *vs.* 100% for S-analogues **10**).[145] The lower yields of vinyl ethers may be caused by the use of a weaker base. A non-polar solvent, for example, benzene, leads to a decrease in the product yields even in the presence of a strong base.[146] In the case of vinyl sulfides, elimination occurs too easily; therefore, this effect cannot be detected for sulfur-containing substrates; it is even possible to use potassium pentoxide in pentyl alcohol[147 – 149] or in THF.[150]

Scheme 43

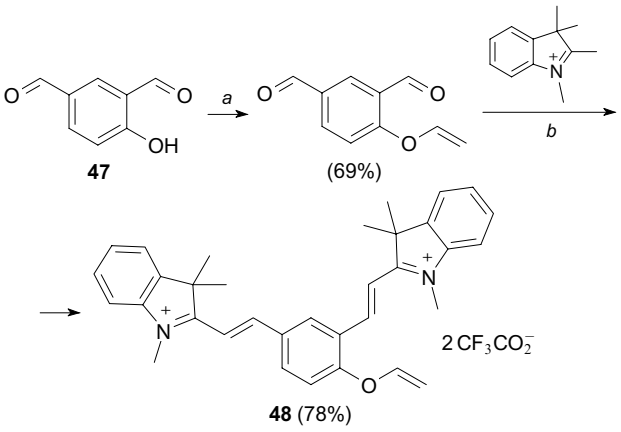


(*a*) KOBu^t, Bu^{t}OH, Δ; (*b*) NaOEt, EtOH, Δ; X = O (**5**), S (**10**); R = H, Me, Cl, NO_2, OMe

Phase transfer catalysts, for example, tetra-n-butylammonium hydrogen sulfate, are also suitable for the preparation of vinyl ethers.[151] In this two-phase system, the product yields increase to 97%. Probably, the ethers migrate to the organic phase (benzene), which prevents their subsequent decomposition. The elimination reaction (unlike the nucleophilic addition to acetylene) is tolerant to the presence of electron-withdrawing substituents in the substrates. For example, vinyl *p*-nitrophenyl ether was obtained by refluxing *p*-(2-bromoethoxy)nitrobenzene in the presence of a base in *tert*-butyl alcohol.[152] Aldehyde groups do not interfere with this reaction either.

4-Hydroxyisophthalaldehyde (**47**) was successfully vinylated in order to prepare salt **48** (Scheme 44).[153] During the product isolation by column chromatography, trifluoroacetic acid (TFA) was added to the eluent.

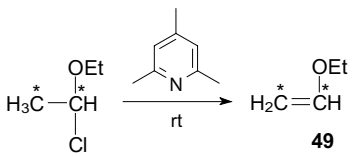
Scheme 44



(*a*) 1) $Br(CH_2)_2Br$, K_2CO_3, MeCN, 70 °C, 12 h; 2) KOBu^t, THF, –40 °C, 30 min; (*b*) 1) Ac_2O, NaOAc, 80 °C; 2) TFA

Dehydrochlorination of α-chloro derivatives has not found wide use in the synthesis of vinyl ethers. Only some specific cases of this reaction can be noted, for example, the synthesis of labelled vinyl ethyl [1,2-^{14}C]-ether **49** (Scheme 45; the ^{14}C isotope is asterisked).[154] This ether was used in the intermediate step of the synthesis of labelled malondialdehyde, which is a marker of lipid peroxidation and oxidative stress in the body.[155] It is surprising that in the presence of pyridine as the base, the yield of the labelled ether decreased to 15%,[154] whereas the non-labelled ether was prepared by this procedure in a yield of 43% (after

Scheme 45



distillation).[156] For increasing the product yield, the authors proposed to replace pyridine by 2,4,6-collidine. The issue of the dependence of the outcome of elimination on the strength of the base at ^{14}C atoms remains open.

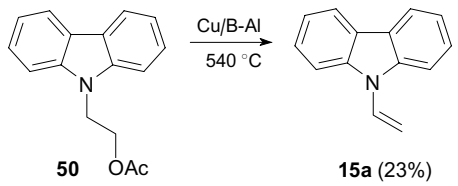
The use of potassium fluoride supported on alumina as the base in elimination reactions is unusual.[157] In this case, the yield of vinyl phenyl ether reaches 73% (after all purification stages) with tetraglyme being used as the solvent. On the one hand, supported potassium fluoride is a solid base, it can be reused many times and cannot get into the reaction mixture. On the other hand, potassium fluoride is soluble in water traces present in the solvents; therefore its content would decrease with time. In addition, this base is a mechanical mixture of alumina and potassium fluoride thoroughly dried in vacuum; therefore, the reaction mixture should be purified from inorganic impurities.

Dehydration is a special case of elimination reaction. In this case, β-hydroxyethyl derivatives are used as the starting compounds. The range of dehydrating agents is fairly narrow. The vinyl ethers formed in the reaction are stable only in an alkaline medium. In an acid medium, they are immediately hydrolyzed to give initial alcohols and acetaldehyde; this is accompanied by polymerization or copolymerization. This process can be suppressed by the use of resins and molecular sieves.[158] For example, heating of a reaction mixture consisting of β-hydroxyethylbenzenethiol, a commercially available acidic resin and 3 Å molecular sieves afforded phenyl vinyl sulfide (**10a**) in 97% yield. It is noteworthy that not any vinyl derivative is stable under these conditions.

The preparation of vinyl ethers (8 examples) and *N*-vinylpyrrolidone (**16**) is also possible in the gas phase.[140] Alkali and alkaline earth metal oxides are employed as dehydrating agents. The reactions take place at high temperatures (350–430 °C) in the presence of SiO_2. The best conversion (81%) was attained with Cs_2O.[159] Most likely, water that is formed in the dehydration reacts with metal oxide to give alkali, which is also hygroscopic. Considering the amount of the oxide used, this reaction can hardly be called catalytic.

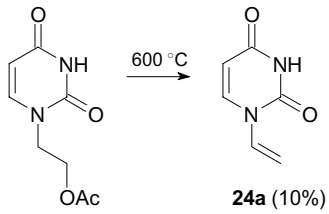
The decomposition of *N*-(2-acetoxyethyl) derivative **50** to give *N*-vinylcarbazole (**15a**) can be classified as an elimination reaction (Scheme 46). This reaction occurs in the gas phase on alumina in the presence of phosphorus oxide[160] or in a column packed with copper borate–alumina pellets at a reduced pressure (3–20 mm Hg).[161]

Scheme 46



High-temperature pyrolysis of *N*-(2-acetoxyethyl)uracil furnishes vinyl derivative **24a** in a low yield at a moderate conversion of the substrate (Scheme 47).[132] In view of high temperature, reduced pressure and 10% yield of the product, this method is regarded to be insufficiently efficient.

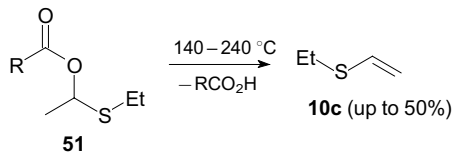
Scheme 47



The yields of *N*-vinylpyrazoles, -imidazoles and -triazoles obtained in a similar way were increased to 60% by addition of water. In this case, too, the acetates of N-ethyl-substituted heterocycles were used as the starting reactants (see Scheme 46).[162] The reactants were pyrolyzed at temperatures of about 350–400 °C. The addition of water was found to prevent resin formation. *N,N*-Divinylaniline can also be obtained in a 70% isolated yield by the pyrolysis of *N,N*-bis(2-trimethylammonioethyl)aniline hydroxide (a quaternary ammonium hydroxide) in an inert atmosphere at 150 °C.[163]

Pyrolysis of the acyloxy or benzoyloxy derivatives of aliphatic sulfides **51** affords carboxylic acids and vinyl ethyl sulfide (**10c**) in a moderate yield (Scheme 48).[164]

Scheme 48

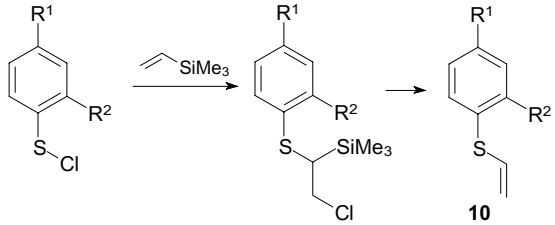


R = Me, Ph

A similar process occurs for heterocycles: for example, pyrolysis of 1-(1-acetoxyethyl)pyrrole gives *N*-vinylpyrrole in 65% yield.[165] Benzoyloxy derivatives are preferred in this reaction, because the separation of acetic acid from the final mixture is more difficult.

Silicon-containing adducts **52** were prepared by treating arylsulfenyl chlorides with vinyltrimethylsilane.[166] It has been assumed that these adducts can eliminate Me_3SiCl or HCl, because β-chloro sulfides and β-chloro silanes are relatively labile.[167,168] Compounds **52** turned out to be rather stable; on solvolysis in ethanol or on treatment with potassium fluoride in various solvents or with silver trifluoroacetate, they gave substituted aryl vinyl sulfides **10** in up to 99% yields (Scheme 49).

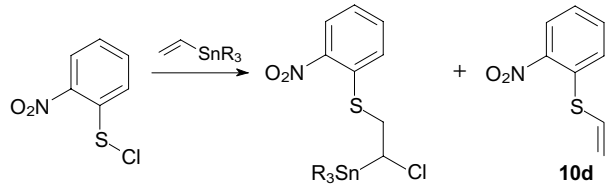
Scheme 49



R¹, R² = NO_2, Cl, Me

The authors presented a mechanism of vinyl sulfide formation, relying on previous studies of the reaction of vinylstannanes with sulfenyl chlorides, which resulted in the synthesis of vinyl sulfide **10d** (Scheme 50).[169, 170]

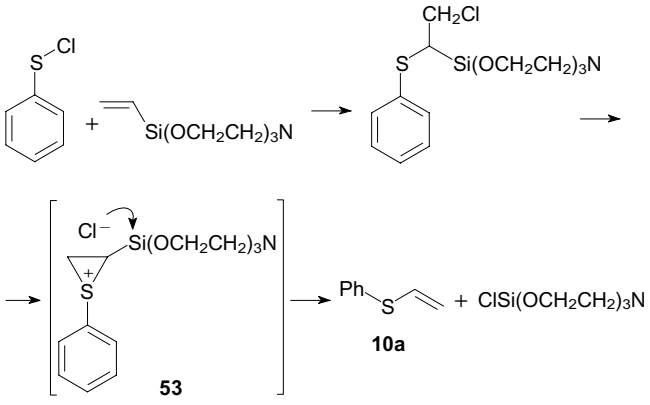
Scheme 50



By oxidation of vinyl thioethers **10** with *m*-chloroperoxybenzoic acid (*m*-CPBA), it is possible to prepare the corresponding vinyl sulfoxides. Although at the first glance, the vinyl group is expected to be oxidized to the epoxide group, this does not occur. Moreover, it is known that hydrogen peroxide in acetic acid oxidizes phenyl vinyl sulfide (**10a**) to give vinyl sulfone.[171] This stability of the vinyl group opens up prospects for the synthesis of unsymmetrical sulfoxides and epoxides. The initial method based on elimination of trimethylsilyl chloride (see Scheme 49) has not been later widely employed, probably, because of the necessity to use difficult-to-obtain vinyltrimethylsilane and sulfenyl chlorides and to conduct the reaction at negative temperatures.

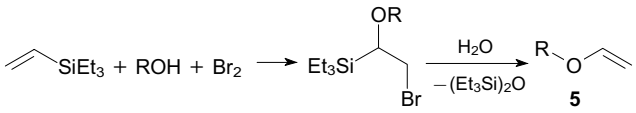
Phenylsulfenyl chloride vigorously reacts with 1-vinylsilatrane (Scheme 51). The resulting adduct **53** is stable only at low temperature, while on heating, it completely decomposes to 1-chlorosilatrane and phenyl vinyl sulfide (**10a**).[172] Generally, sulfenyl chlorides are relatively reactive: for example, in dichloromethane, even at −78 °C, phenylsulfenyl chloride transforms thioacetals and thioketals into the corresponding α-chloro sulfides, which are converted to vinyl sulfides *via* elimination of HCl.[173]

Scheme 51



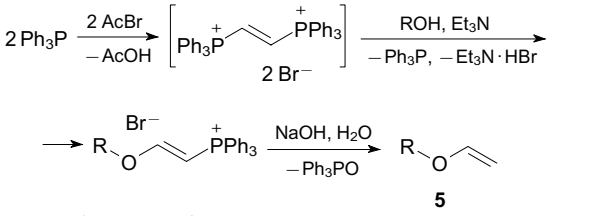
Vinylsilanes react not only with sulfenyl chlorides.[174] In alcohol solutions of bromine, they form alkyl vinyl ethers and disiloxanes (Scheme 52). Unlike the former two methods involving organosilicon substrates (see Schemes 49 and 51), this procedure can be regarded as a preparative pathway to vinyl ethers **5** (the product yields are 60% – 70%).

Scheme 52



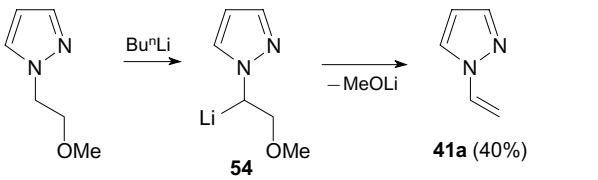
Elimination of phosphonium salts from unsaturated compounds also leads to vinyl ethers in 50% to 76% yields.[175] The reaction comprises several steps and generates numerous side products (including phosphorus compounds) in noticeable amounts (Scheme 53). It is noteworthy that the replacement of protium atoms in the $NaOH-H_2O$ system by deuterium results in the formation of vinyl ethers with the $O-CH=CD_2$ moiety. The condensation of two phosphonium salt molecules followed by elimination of the phosphorus-containing group afforded benzyl-*N*-[1-(benzyloxycarbonylamino)ethyl]-*N*-vinylcarbamate (33% yield).[176]

Scheme 53



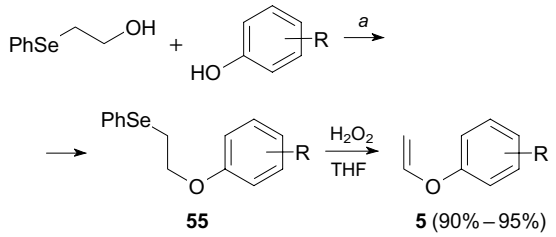
Elimination of lithium methoxide from lithium intermediate **54** gave *N*-vinylpyrazole (**41a**) in 40% yield (Scheme 54).[177] This outcome was unexpected for the authors, but it was fully consistent with experimental data on metallation of pyrazoles.[178, 179] The same mechanism may be involved in the formation of phenyl vinyl sulfide (**10a**) from 1,2-bis(phenylthio)ethane in the presence of n-butyllithium in the HMPA – THF system (52% yield).[180]

Scheme 54



On treatment with hydrogen peroxide, β-selenoethyl derivatives **55** undergo oxidative elimination, giving rise to vinyl ethers **5** (Scheme 55).[181] The starting selenium derivatives are prepared by alkylation of phenols with β-phenylselenoethanol in the presence of triphenylphosphine and diethyl azodocarboxylate (DEAD).[182] β-Selenoethanol is formed smoothly in the reaction of readily obtainable diphenyl diselenide with sodium hydride followed by the addition of 2-chloroethanol. In view of high yields and a rather broad range of reaction products, this method can be considered to be quite efficient. The syntheses of aryl vinyl ethers from β-phenylselenoethanol attached to a polystyrene matrix were performed in a similar way (by oxidative

Scheme 55



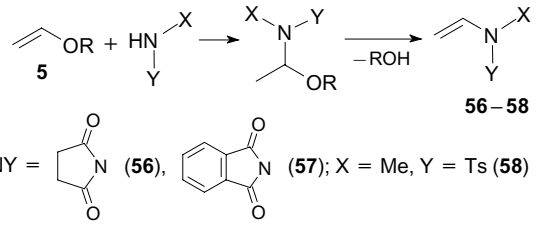
55 **5** (90%–95%)

(*a*) Ph_3P, DEAD, Pr^i_2NEt, THF, rt; R = H, Alk, Hal, NO_2, CN, CO_2Me, Ar (in different positions)

elimination).[183, 184] 2-(Phenylsulfonyl)ethanol can also be used as the starting alcohol in the solid-phase syntheses.[185]

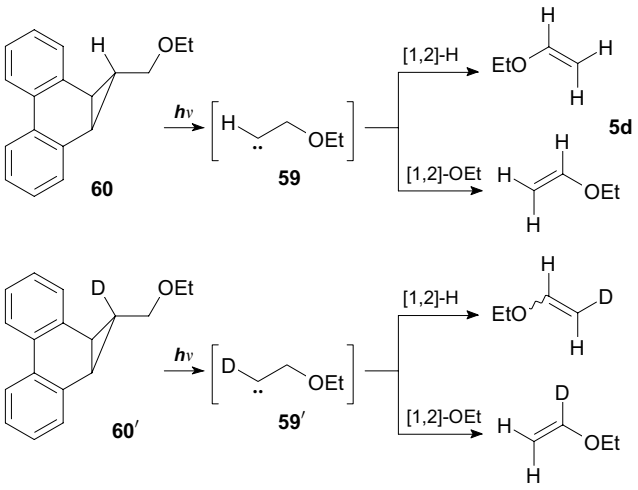
Vinyl ethers can be used as the starting compounds for the synthesis of N-vinyl derivatives (Scheme 56). In the first step, these substrates are reacted with acid imides to give α-imidoethers, which eliminate alcohol in the presence of acid catalysts to give *N*-vinylimides.[186] *N*-Vinylsuccinimide (**56**), -phthalimide (**57**) and -*N*-methyl-*p*-toluenesulfonamide (**58**) were synthesized in this way in up to 90% yields.

Scheme 56



The rearrangement of the simplest carbene, 2-ethoxyethylidene (**59**), generated photochemically from compound **60**, affords ethyl vinyl ether (**5d**).[187] Since this substrate is fairly exotic, this reaction is not considered as a synthetic route to vinyl ethers (like photodecomposition of 2-ethoxyethyl phenylacetate),[188] but it is quite unusual (Scheme 57). In this case, ethyl vinyl ether can result from the 1,2-hydrogen shift and/or 1,2-shift of the ethoxy group in the carbene, *i.e.*, two possible reaction pathways are considered.

Scheme 57

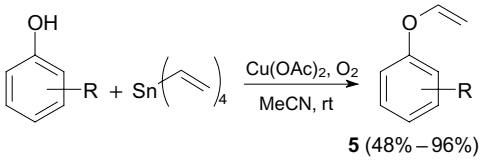


Experiments with deuterium-labelled carbene show that the 1,2-hydrogen shift is preferable for carbene **59′**, which has been confirmed by theoretical calculations. On exposure to visible light, substituted vinyl thioethers can also be synthesized in considerable amounts.[189]

5. Cross-coupling reactions

O-, S- and N-vinyl derivatives can be obtained using copper- and palladium-catalyzed carbon–heteroatom cross-coupling reactions. A procedure has been developed for the synthesis of aryl vinyl ethers **5** by copper(II) acetate-catalyzed C–O coupling of phenols with tetravinyltin (Scheme 58).[190]

Scheme 58

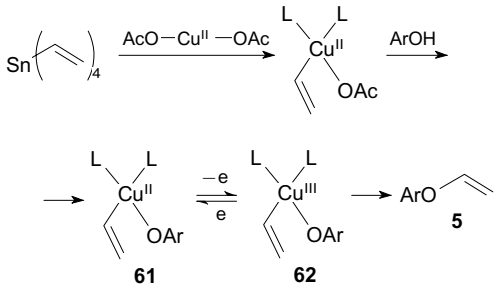


5 (48%–96%)

R = 4-Ph, 3-Ph, 2-Ph, 4-OMe, 4-CN, 4-NO_2, 4-CO_2Me, 4-NHAc, 4-$CH_2CH(NHBoc)CO_2Me$; Boc is *tert*-butoxycarbonyl

The reaction proceeds under mild conditions and gives products **5** in good yields to excellent yields. High conversion of the starting compound can be attained in an oxygen atmosphere. This is consistent with the reaction mechanism proposed by the authors, comprising an attack of the intermediate vinyl copper compound by phenol, oxidation of the resulting phenoxide **61** to copper(III) derivative **62** and the subsequent reductive elimination of aryl vinyl ether 5 (Scheme 59, L is any ligand).

Scheme 59

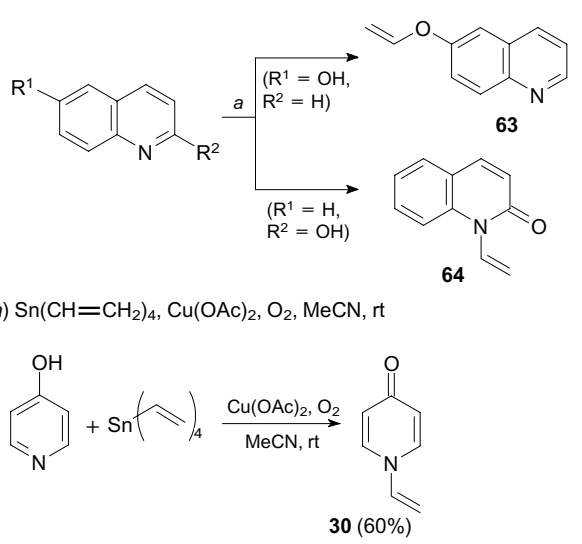


L is ligand

It is noteworthy that the amide nitrogen atom in the substrate side chain is not affected in this reaction; however, in the presence of a nitrogen atom incorporated in the ring of the starting compound, both O- and N-vinylation is possible. 6-Hydroxyquinoline is selectively vinylated at the oxygen atom to give vinyl ether **63**, whereas 2-hydroxyquinoline and 4-hydroxypyridine give the products of vinylation at the nitrogen atom — compounds **64** and **30**, respectively (Scheme 60).

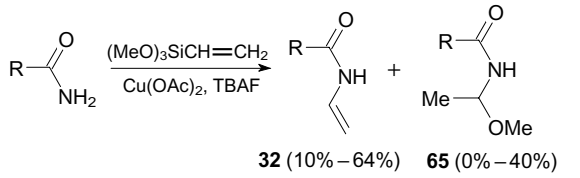
A procedure for N-vinylation of amides with vinyltrimethoxysilane[191, 192] in the presence of $Cu(OAc)_2$ and tetra-n-butylammonium fluoride (TBAF) has been devel-

Scheme 60



oped (Scheme 61). The target products **32** are formed in moderate yields; in some cases, the reaction is complicated by the formation of (1-methoxyethyl)amides **65** as side products. The temperature and solvent of choice for the reaction depend on the nature of the substrate and were specially selected for each case. The best results were attained in dichloromethane, dimethylformamide or dioxane at room temperature or on heating to 50 °C. The highest yields (51% – 64%) without the formation of side products were attained for substrates with R = Ph, 2-Py, 4-Py, 3-PyCH=CH.

Scheme 61



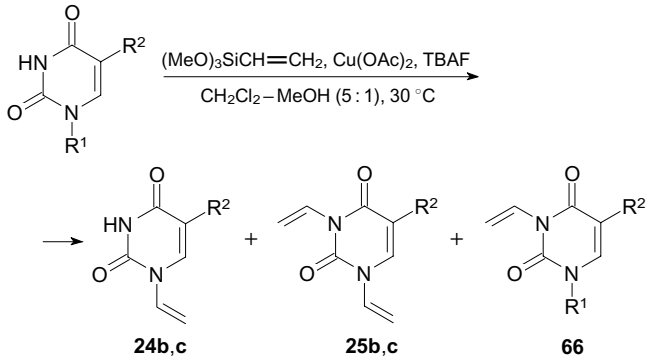
R = Ph, PhCH=CH, 2-Py, 2-PyCH=CH, 3-Py, 3-PyCH=CH, 4-Py, 4-PyCH=CH, 3,4,5-$Me_3C_6H_2$, 4-$O_2NC_6H_4$, 2-Th;
Py is pyridyl, Th is thienyl

The same procedure with minor modifications can be used for vinylation of a nitrogen atom incorporated in a five- or six-membered ring. This approach has been employed [193] for the synthesis of N-vinylated nitrogenous bases and nucleosides (Scheme 62). In the case of 5-methyl- and 5-fluorouracils, only products **24b**,**c** and **25b**,**c** are formed, while N(1)-substituted analogues are vinylated at the N(3) atom to give compounds **66**.

A similar procedure has been used [193] to prepare *N*-vinylphthalimide (**57**) and vinylated five-membered nitrogen heterocycles — indole (**13a**), imidazole (**67**) and benzimidazole (**68**) (Scheme 63).

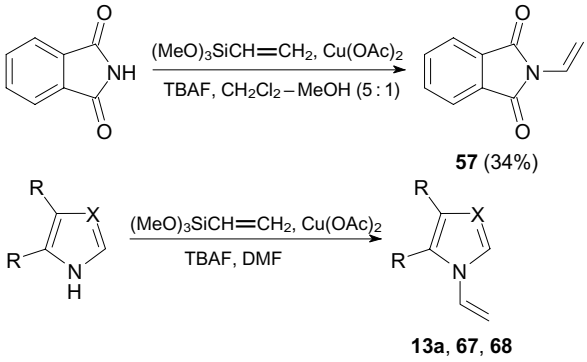
Vinyltrimethoxysilane and the system consisting of copper, iron(III) chloride and TBAF as the catalyst have also been used for vinylation of five-membered nitrogen heterocycles (Scheme 64).[194] Like in the study cited above,[193] the

Scheme 62



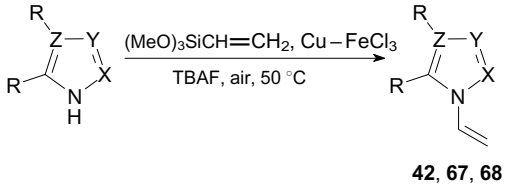
R^2	R^1	Yield of **24** (%)	Yield of **25** (%)	Yield of **66** (%)
F	H	27	33	–
Me	H	22	25	–
F	Tetrahydrofuran-2-yl	–	–	47
H	β-D-Ribofuranosyl	–	–	74
Me	2-Deoxy-β-D-ribofuranosyl	–	–	81

Scheme 63



X = N: R = H (**67**, 38% yield), R – R is benzo (**68**, 60%);
X = CH, R – R is benzo (**13a**, 50%)

Scheme 64

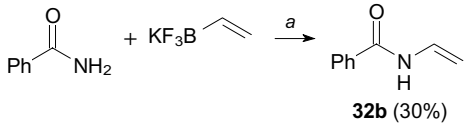


R = H: X = CH, Y = N, Z = C (**67**, 41% yield);
X = Z = N, Y = CH (**42**, 60%); X = CH, Y = N,
Z = C, R – R is benzo (**68**, 66%)

yields of *N*-vinylheterocycles **42**, **67** and **68** were moderate. The benefits of this procedure are the conduction of the reaction without a solvent and with only 3 mol.% Cu and $FeCl_3$, whereas in all of the above-described procedures, an equimolar amount of the catalyst is used.

Another possible source of the vinyl group in C–N coupling reactions is potassium vinyl trifluoroborate. It was used to vinylate benzamide;[195,196] however, the yield of the target product **32b** was relatively low (Scheme 65).

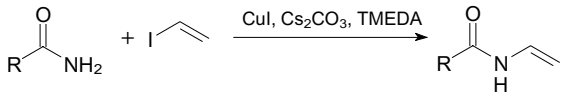
Scheme 65



32b (30%)

(*a*) $Cu(OAc)_2$ (10 mol.%), CH_2Cl_2–DMSO (1 : 1), O_2, MS 4 Å, 40 °C, 20 h; MS are molecular sieves

Scheme 66



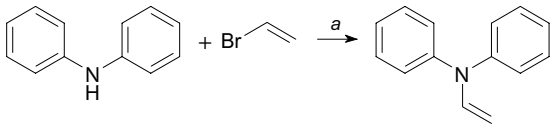
32c,**d**

R = (*E*)-PhCH=CH (**c**, 50% yield), $MeOCH_2$ (**d**, 56%); TMEDA is tetramethylethylenediamine

N-Vinylamides **32c**,**d** have also been obtained by the copper(I) iodide-catalyzed C–N-coupling of appropriate amides with vinyl iodide (Scheme 66).[197]

The palladium-catalyzed cross-coupling has not found wide use for the synthesis of O-, S- or N-vinyl derivatives with an unsubstituted vinyl group. Currently, only three publications devoted to this approach are known. An example of C–N coupling of diphenylamine with vinyl bromide has been reported[198] (Scheme 67). The reaction conditions are standard and product **69a** is formed in a good yield.

Scheme 67



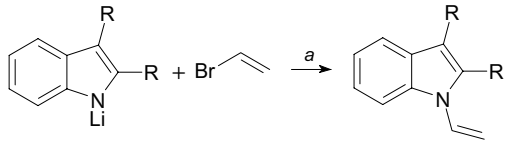
69a (86%)

(*a*) $Pd_2(dba)_3$, PBu^t_3, $NaOBu^t$, PhMe, 90 °C; dba is dibenzylideneacetone

A method for palladium-catalyzed *N*-vinylation of pyrrole, indole, carbazole and their derivatives using alkenyl bromides has been proposed.[199] Altogether 16 products were obtained in 30%–99% yields, including indole (**13a**) and carbazole (**15a**) derivatives with an unsubstituted vinyl group (Scheme 68). The authors noted that for increasing the product yield, the initial N-heterocycle should be pretreated with n-butyllithium to be converted to the corresponding lithium derivative.

An unusual method for the synthesis of aryl vinyl sulfides **10** has been recently developed based on palladium-catalyzed C–S-coupling of aryl bromides with 2,2-diphenyl-1,3-oxathiolane (**70**), which acts as an equivalent of vinyl sulfide in the presence of the Pd-Xantphos G3 (**71**)

Scheme 68

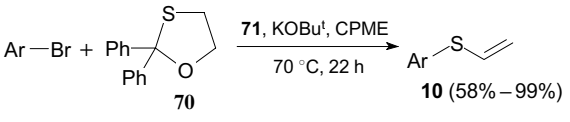


13a, **15a**

(*a*) $Pd(dba)_2$, PBu^t_3, PhMe, DME, 85–90 °C; R = H (**13a**, 61% yield); R–R is benzo (**15a**, 59%); DME is dimethoxyethane

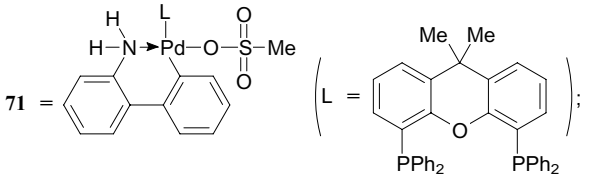
catalyst (Scheme 69).[200] The procedure is applicable to a broad range of aromatic compounds, including various benzene, naphthalene and quinoline derivatives and gives products in high yields (>80%) for most substrates. The mechanism proposed by the authors includes generation of the $CH_2{=}CH{-}S^-$ anion, involved in the C–S-coupling reaction, *via* cleavage of oxathiolane **70** under the action of

Scheme 69



70

10 (58%–99%)



Ar is substituted phenyl, biphenyl, naphthyl, quinolinyl; CPME is cyclopropyl methyl ether

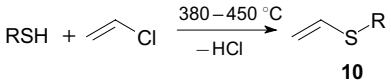
a base and the usual Pd^0/Pd^{II} catalytic cycle.

6. Miscellaneous methods

6.1. Substitution reactions

Vinyl chloride reacts with arene thiols and thiophene-2-thiol in the gas phase under atmospheric pressure and temperatures up to 450 °C to give vinyl sulfides **10** in up to 70% yields.[201] A selective reaction requires a 12–200-fold excess of vinyl chloride (Scheme 70). This reaction is possible, because it gives low-molecular-weight hydrogen chloride, which is energetically favourable.

Scheme 70

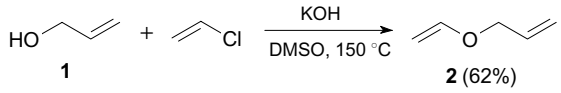


10

R = Ar, 2-Th

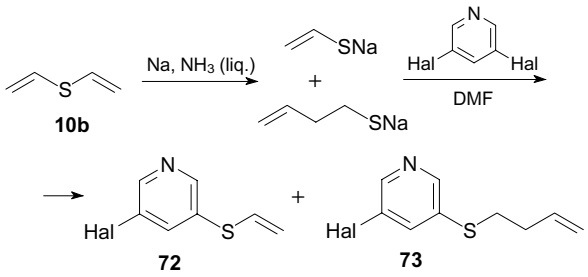
Most likely, free-radical processes also take place at this temperatures, which results in relatively low product yields. A process of this type is also possible in solution. For example, allyl vinyl ether (**2**) can be obtained in a superbasic medium from vinyl chloride and allyl alcohol (**1**) (Scheme 71).[202] This reaction is rather unusual, as elimination rather than substitution should be expected in a superbasic medium.

Scheme 71



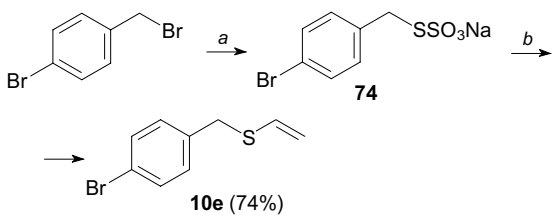
Divinyl sulfide (**10b**) can also be used as a source of the vinyl group. For example, on treatment with sodium metal in liquid ammonia, it is converted to two thiolates, which undergo the classical nucleophilic substitution reaction with halo derivatives to give the corresponding sulfides. For example, the reaction with 3,5-dihalopyridine gives products **72** and **73** in a ratio from 1 : 1 to 1 : 5 and in a total yield of 30% – 70% (Scheme 72).[203] This procedure is applicable for the preparation of not only aromatic, but also aliphatic ethers (for example, in the reaction with n-butyl bromide). The major drawback of this method is the formation of product mixtures that the authors failed to isolate.

Scheme 72



The reaction of the Grignard reagents with the Bunte salts (**74**) is a thiol-free method for the preparation of sulfides (Scheme 73).[204] The Bunte salts are crystalline compounds; they are prepared rather readily and do not have a strong smell (unlike thiols), that is, the procedure is convenient. The researchers present quite a few examples of the synthesis of sulfides with varied aryl halides and Grignard reagents. As an example, consider the synthesis of vinyl derivative **10e** (it is a single example).

Scheme 73

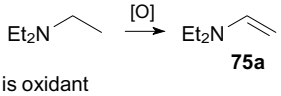


(*a*) $Na_2S_2O_3$, MeOH, H_2O, 65 °C, 1 h;
(*b*) $CH_2{=}CHMgCl$, THF, 0 °C → rt, 30 min

6.2. Oxidation of the ethyl group

The ethyl group of triethylamine can be chemically [205 – 207] or photochemically [208, 209] oxidized to the vinyl group to give compound **75a** (Scheme 74). The oxidants used for this purpose include benzoyl peroxide,[205] iodine,[206] *N*-bromosuccinimide,[207] hexachloroethane [208] and 2,2-dimethyl-3,4-dihydro-2*H*-benzo[*h*]chromene-5,6-dione;[209] however, these procedures are not used for preparative purposes as yet.

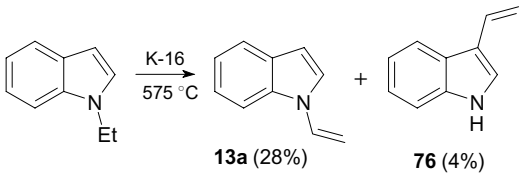
Scheme 74



[O] is oxidant

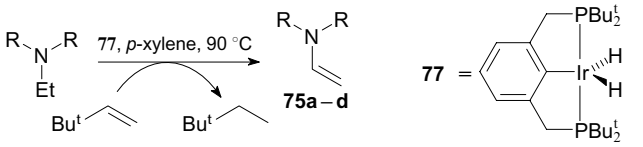
N-Vinylindole (**13a**) has been synthesized by catalytic dehydration of *N*-ethylindole (Scheme 75).[210] The reaction is carried out in a flow reactor on the commercial K-16 catalyst based on iron and chromium oxides. The yield of vinylindole **13a** is relatively low due to the low conversion of the initial compound; this is also accompanied by partial isomerization of the product to 3-vinylindole (**76**).

Scheme 75



Later,[211] a method has been proposed for dehydration of tertiary amines in the presence of iridium complex **77** as the catalyst and *tert*-butylethylene as the hydrogen acceptor (Scheme 76). A possible complication of this procedure is dehydration of several alkyl groups, resulting in a mixture of products. However, as noted by the authors, this trouble can be avoided by selecting the optimal reactant ratio and reaction time. An exception is 1-ethylpyrrolidine, the dehydration of which is accompanied by aromatization of the heterocycle to give *N*-vinylpyrrole (67% yield).

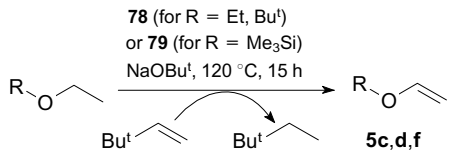
Scheme 76



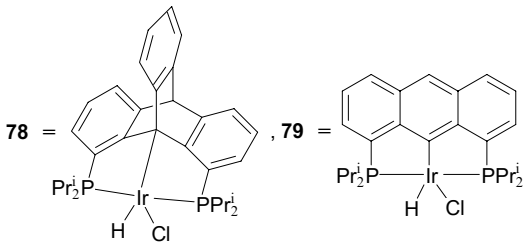
R = Et (**a**, 65% yield), Me (**b**, 65%), Pr^i (**c**, 98%);
R – R = $(CH_2)_3$ (**d**, 35%)

A similar procedure has been used for dehydration of the ether ethyl group to give products **5c**,**d**,**f** (Scheme 77).[212] The reaction is carried out under more drastic conditions than those used with amines; the active catalyst is generated *in situ* by the base-induced dehydrohalogenation of complex iridium hydrochlorides **78** or **79**. Norbornene [211] and ethylene [212] can also be used, apart from *tert*-butylethylene, as hydrogen acceptors in the catalytic dehydration of amines and ethers.

Scheme 77



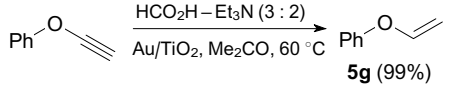
R = Et (**d**, 47% yield), Bu^t (**c**, 50%), Me_3Si (**f**, 55%)



6.3. Reduction of acetylenes

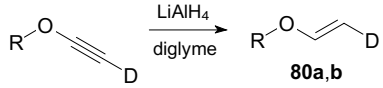
Ethynyloxybenzene (phenoxyacetylene) was converted to phenyl vinyl ether (**5g**) in an almost quantitative chromatographic yield.[213] A mixture of formic acid and triethylamine was used as the reducing agent and gold nanoparticles supported on titanium dioxide served as the catalyst (Scheme 78).

Scheme 78



Deuterium-labelled vinyl ethers **80a**,**b** are formed upon the reduction of appropriate deuteroalkynes with lithium aluminium hydride in diglyme.[15,214] In both cases, vinyl derivatives with *E*-configuration of the double bond are formed (Scheme 79).

Scheme 79

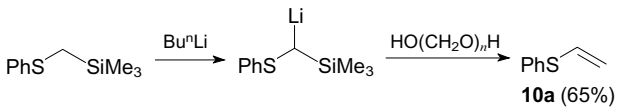


R = Et (**a**, 51% yield), Ph (**b**, 33%)

6.4. Peterson reaction

A special case of Peterson alkenylation has been reported: namely, the reaction of phenylthio(trimethylsilyl)methyllithium with paraformaldehyde,[215,216] which results in the formation of phenyl vinyl sulfide (**10a**) (Scheme 80).

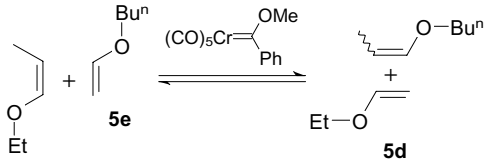
Scheme 80



6.5. Metathesis reactions

The metathesis reactions involving vinyl ethers are potentially applicable for interconversion of various vinyl ethers. The reaction of ethyl *cis*-propenyl ether with n-butyl vinyl ether (**5e**) in the presence of a chromium carbene complex has been studied (Scheme 81).[217]

Scheme 81

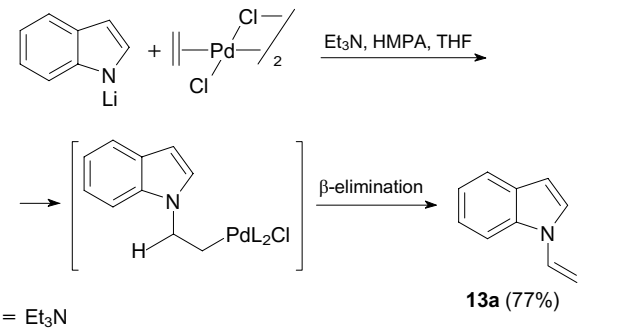


In this case, the formation of only alkenyl alkyl ethers was established; no other possible products (*e.g.*, RO–CH=CH–OR and R–CH=CH–R, where R = Et, Bu^n) were found in the reaction mixture. The reaction is equilibrium and the product distribution is statistical, that is, all four ethers are present in the reaction mixture in equimolar amounts. The reaction was also accompanied by *cis*–*trans* isomerization of the double bond, with the contents of *cis*- and *trans*-propenyl ethers in the final mixture being close to statistical values: 57% of *cis*-isomers for both compounds.

6.6. Ethylene insertion into the metal–nitrogen bond

N-Vinyl derivatives can be obtained *via* ethylene insertion into the metal–nitrogen bond of N-lithium compounds followed by β-elimination of the hydride complex. The reaction of an ethylene–palladium chloride complex with indolelithium, giving rise to *N*-vinylindole, has been reported[218] (Scheme 82).

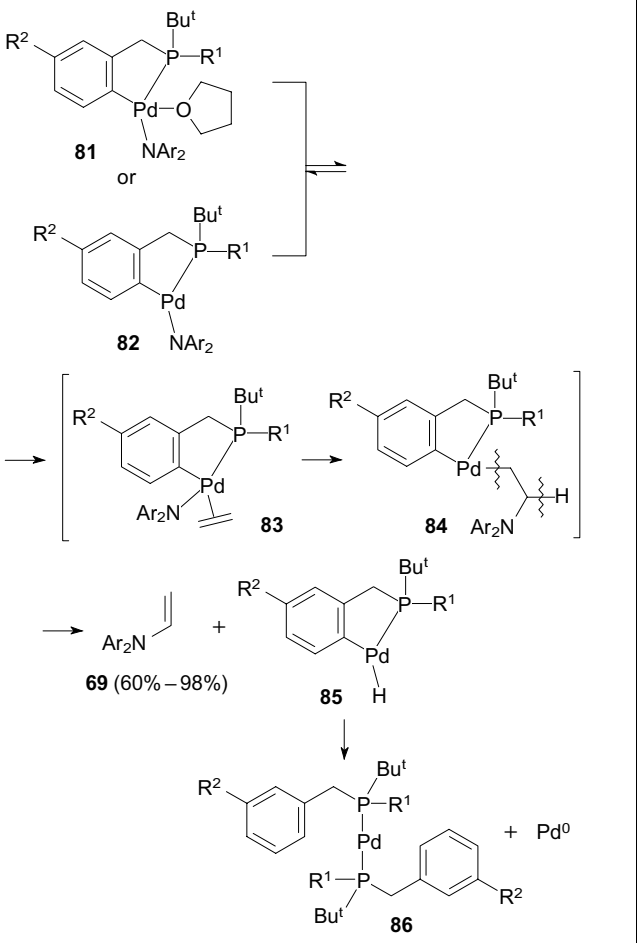
Scheme 82



L = Et_3N

Later, Hartwig's research group[219,220] studied the ethylene insertion into the Pd–N bond using complexes **81** and **82** (Scheme 83). The reaction mechanism proposed by the authors includes the migration insertion of ethylene into the Pd–N bond of intermediate complexes **83** to give alkylpalladium intermediates **84**. The subsequent β-elimination affords *N*-vinyldiarylamines **69** and complexes **85**, which are cleaved with C–H bond formation to compounds **86** and palladium black.

Scheme 83



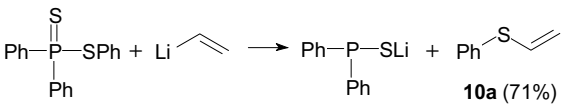
For **81:** Ar = Ph, 4-MeOC$_6$H$_4$, 4-MeC$_6$H$_4$, 4-FC$_6$H$_4$, 3,5-(F$_3$C)$_2$C$_6$H$_3$; for **82:** Ar = Ph; R^1 = Pr^i, Bu^t; R^2 = H, F$_3$C, MeO

6.7. Synthesis based on organometallic compounds

A convenient vinylating agent is vinyllithium, which can be obtained rather easily by exchange reaction between phenyllithium and tetravinyllead in diethyl ether or by metal exchange reaction between lithium and tetravinyllead or tetravinyltin.[221] Vinyllithium is a fairly reactive compound: indeed, it reacts with diphenylphosphinodithioates to give sulfides in up to 94% yield.[222]

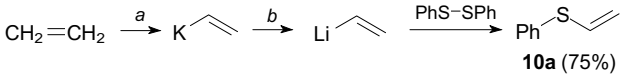
In particular, phenyl vinyl sulfide (**10a**) can be obtained in a moderate yield in a reaction involving vinyllithium (Scheme 84).[222]

Scheme 84



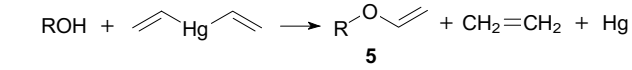
The reaction of vinyllithium with diphenyl disulfide also gives phenyl vinyl sulfide (Scheme 85).[223] In this case, vinyllithium can be prepared directly from ethylene, which eliminates the need for handling toxic lead and tin organic compounds.

Scheme 85



(*a*) Bu^{n}Li, KOBu^t, TMEDA, hexane, –25 °C; (*b*) LiBr, THF

Scheme 86



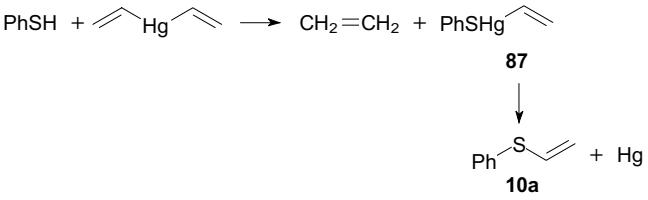
R = Ar, Het

Inorganic and organic acids decompose organomercury compounds rather easily. Phenols possess sufficient acidity to react with divinylmercury to give aryl vinyl ethers **5** (85% – 96% yields), ethylene and mercury metal (Scheme 86).[224]

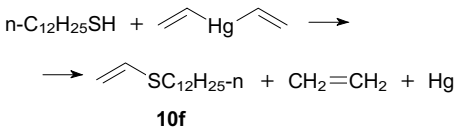
A similar reaction of vinylmercury with benzenethiol affords mercury-containing derivative **87**, which decomposes on further heating to vinyl thioether **10a** and mercury (Scheme 87).[224]

Aliphatic thiols (for example, dodecanethiol) react with divinylmercury on heating to 115 °C to give sulfides (in particular, **10f**) (Scheme 88).[224]

Scheme 87

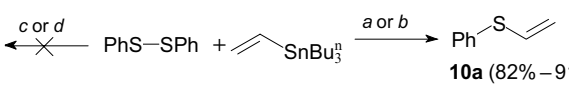


Scheme 88



Free-radical substitution reactions of mercury and tin organic derivatives with diphenyl disulfides give the corresponding vinyl sulfides in up to 91% yields.[225] During the reaction, upon irradiation with light or under the action of a classical free-radical initiator, azobis(isobutyronitrile) (AIBN), the starting diphenyl disulfides are converted to reactive species, which then attack organometallic reagents. Although the reaction includes several steps, in particular, addition and elimination steps, the free-radical mechanism

Scheme 89

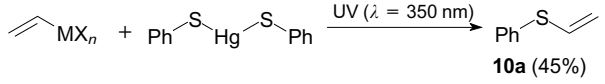


(*a*) *hv*, 4 h; (*b*) AIBN (0.1 equiv.), 80 °C, 4 h; (*c*) dark, 50 °C, 4 h; (*d*) *hv*, Bu$^t_2$NO (0.15 equiv.), 2 h

is confirmed by the absence of reaction products without initiators or initial irradiation (Scheme 89).

The range of possible participants of this reaction is rather wide and implies the use of both various substrates (disulfides, sulfonyl chlorides and selenides) and various organometallic reagents (mercury and tin derivatives) (Scheme 90).

Scheme 90

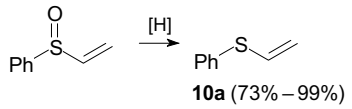


MX$_n$ = HgCl, SnBu$^n_3$

6.8. Reduction of *S*-vinyl sulfoxides

The reduction of the S=O group of vinyl sulfoxides can be considered as an approach to the synthesis of vinyl sulfides. Quite a few publications [226 – 248] are devoted to the reduction of sulfoxides to sulfide and consider, in particular, the synthesis of phenyl vinyl sulfide (**10a**) from phenyl vinyl sulfoxide (Scheme 91).

Scheme 91

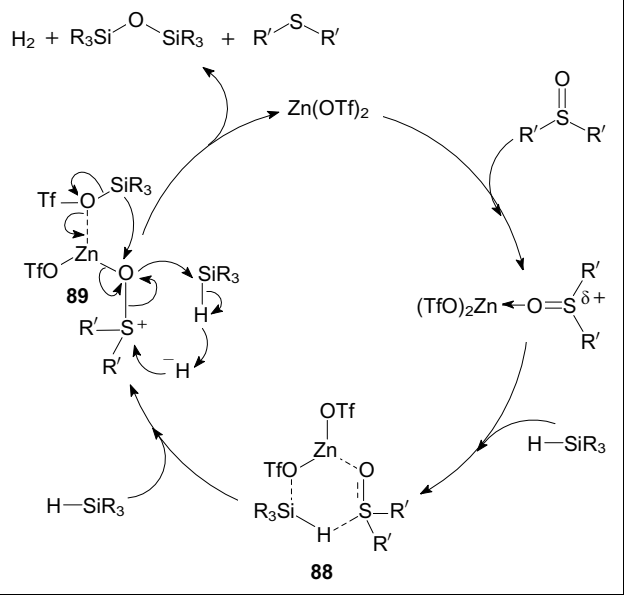


[H] is reducing agent

Most of the procedures are catalytic and can be conducted with diversified reducing agents. Most often, phenylsilane ($PhSiH_3$) is used [226 – 232] with catalysts such as $Zn(OTf)_2$ [OTf is trifluoromethanesulfonate (triflate)],[226] iron complexes,[227, 228] oxorhenium [229 – 231] and oxomolybdenum compounds;[232] it is also possible to use Me_2PhSiH in the presence of gold nanoparticles [233] or $P(OPh)_3$ in the presence of $MoO_2Cl_2(DMF)_2$.[234] The catalyst is necessary in these systems for S=O bond activation, which occurs *via* O-coordination to the metal atom. A catalytic cycle has been proposed [226] for the reduction of vinyl sulfoxides with silanes in the presence of zinc triflate. The reaction proceeds *via* the formation of six-membered transition state **88**, in which zinc triflate is coordinated simultaneously to the S=O group of the substrate and to silane and in which sulfur interacts with the silane hydride atom. Then the reaction with a second silane molecule gives sulfonium salt analogue **89**, which is cleaved to give $(R_3Si)_2O$, hydrogen and zinc sulfide and triflate (Scheme 92).

Low-valence titanium, niobium, tantalum and hafnium can also serve as reducing agents; these species are generated *in situ* in the presence of metals from the corresponding high-valence compounds, for example, in the systems In – $TiCl_4$,[235] In – $NbCl_5$,[236] In – $TaCl_5$,[237] In – Cp_2TiCl_2 (Cp is η-cyclopentadienyl),[238] Ga – Cp_2TiCl_2,[239] Ga – $MoCl_5$ (see [240]) and Zn – $HfCl_4$.[241] Among other reducing agents, mention should be made of thioacetic acid in the presence of iodine,[242] the Fe – H_2O – CO_2 system,[243] 4-methoxybenzyl alcohol [244] and hydrogen [245] in the presence of heterogeneous catalysts and silica gel-supported reducing systems.[246 – 248]

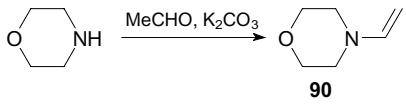
Scheme 92



6.9. Condensation of acetaldehyde with amines

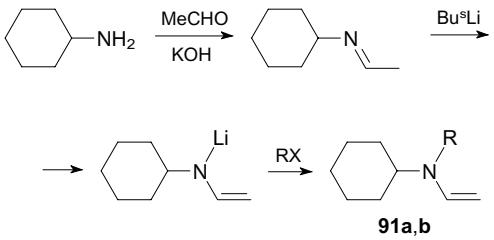
The condensation of secondary amines with aldehydes gives enamines; in the case of acetaldehyde, this results in derivatives with an unsubstituted vinyl group. For example, the reaction of morpholine and acetaldehyde affords *N*-vinylmorpholine (**90**) (Scheme 93).[249]

Scheme 93



Primary amines react with acetaldehyde to give *N*-ethylideneamines, which can be then metallated and alkylated giving rise to tertiary *N*-vinylamines **91a**,**b** in quantitative yields (Scheme 94).[250]

Scheme 94

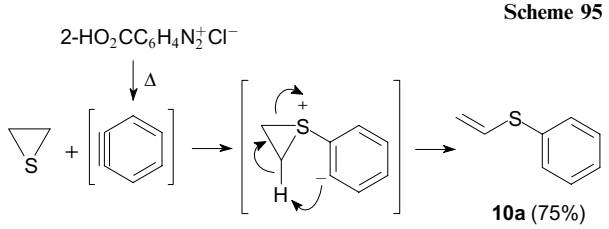


X = I, R = Et (**a**); X = Br, R = Bn (**b**)

6.10. Ring opening

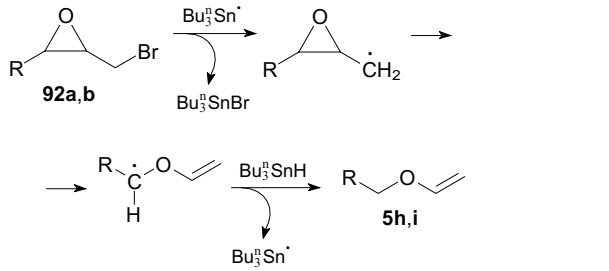
The reaction of thiirane with dehydrobenzene accompanied by three-membered ring opening and giving phenyl vinyl sulfide (**10a**) in a good yield has been reported (Scheme 95).[251]

Scheme 95



Under the action of the AIBN – Bu^n_3SnH system, 2-(bromomethyl)-3-phenyl- (**92a**) and 2-(bromomethyl)-3-(1-naphthyl)oxirane (**92b**) undergo radical elimination of bromine followed by ring opening of the radicals thus formed and results in the formation of ethers **5h**,**i** (Scheme 96).[252]

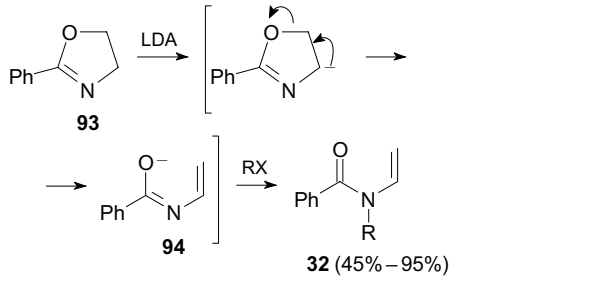
Scheme 96



R = Ph (**92a**; **5h**, 89% yield), 1-Naph (**92b**; **5i**, 92%)

The lithiation of 2-phenyloxazoline (**93**) on treatment with lithium diisopropylamide (LDA) is accompanied by opening of the oxazoline ring forming *N*-vinylbenzamidate anion **94**, which is then alkylated, acylated or hydrolyzed to give *N*-vinylbenzamides **32** in excellent yields for most products (Scheme 97).[253]

Scheme 97

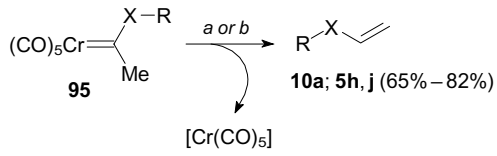


RX = H_2O (for R = H), MeI, EtI, Bu^nBr, BnBr, 2-$BrC_6H_4CH_2Br$, $CH_2{=}CHCH_2Br$, $PhCH{=}CHCH_2Br$, $CH{\equiv}CCH_2Br$, $PhC{\equiv}CCH_2Br$, BzCl

6.11. Cleavage of carbene complexes

Chromium carbene complexes **95** are cleaved, on treatment with pyridine (conditions *a*, for X = S) or in the presence of palladium acetate and triethylamine (conditions *b*, for X = O), giving rise to S- (**10a**)[254] or O-vinyl (**5h**,**j**)[255] derivatives (Scheme 98).

Scheme 98

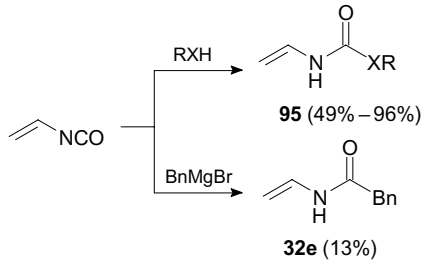


X = S, R = Ph (**10a**); X = O: R = Bn (**5h**), 2-$MeC_6H_4CH_2$ (**5j**)

6.12. Transformations based on vinyl isocyanate

The addition of vinyl isocyanate to alcohols,[197, 256 – 261] thiols,[261] amines[197, 261] or amides[134] is used to prepare *N*-vinylcarbamates, *N*-vinylthiocarbamates and *N*-vinylureas **95**, respectively (Scheme 99). While reacting with organomagnesium compounds, vinyl isocyanate is converted to amides, as has been shown[197] in relation to the reaction with benzylmagnesium bromide, which affords compound **32e** (see Scheme 99).

Scheme 99

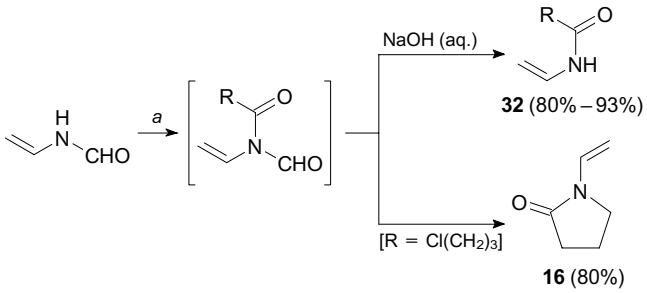


X = O, S, NH; R = Alk, Ar, Acyl

6.13. Preparation of N-vinyl derivatives from *N*-vinylformamide

Recently, a relatively convenient two-step method for the synthesis of *N*-vinylamides **32** from commercially available *N*-vinylformamide has been proposed.[262] The reaction includes acylation of *N*-vinylformamide with acyl chlorides and the subsequent selective hydrolysis of the intermediates thus formed, resulting in the loss of the formyl group (Scheme 100). The use of 4-chlorobutyryl chloride as the acylating agent provides the synthesis of *N*-vinylpyrrolidone (**16**), because in this case, the hydrolysis of the intermediate is accompanied by cyclization (see Scheme 100).

Scheme 100



(*a*) RC(O)Cl, Et_3N, THF; R = Pr^i, Ph, Bu^iO

7. Conclusion

More than 130 years passed since the first studies of A.E.Favorskii dealing with nucleophilic addition to acetylenes. Since then, the range of synthesized vinyl derivatives has been markedly extended, the known procedures have been optimized and new reactions have been developed. The goal of this review is to demonstrate the potential opportunities for the synthesis of compounds containing an unsubstituted vinyl group. Despite the presence of well-established key principles and approaches to the preparation of these derivatives, new methods providing great possibilities are constantly appearing. For example, the replacement of gaseous acetylene by calcium carbide is a promising approach. Calcium carbide is much simpler and safer to handle. In large-scale syntheses, the use of calcium carbide may be beneficial for the countries that do not possess large oil and gas resources (sources for acetylene synthesis), but possess coal and lime (starting compounds for the synthesis of calcium carbide). In the global sense, the replacement of acetylene by the carbide in the syntheses of the key industrial chemicals is a considerable step forward.

The conversion of readily accessible alcohols, thiols and their nitrogen analogues to the corresponding vinyl derivatives using any strategy markedly extends the range of subsequent transformations. The high reactivity of the vinyl group is beyond doubt. However, first of all, mention should be made of its unique potential in the polymer chemistry, which gives rise to particular materials with specified properties. Obviously, most of the obtained vinyl derivatives are now used and will be used as monomers.

The numerous practical applications of S-, O- and N-vinyl derivatives account for the popularity of this class of compounds among organic chemists. However, the synthetic potential of the vinyl group has not been fully appreciated. For example, its protecting function is obviously underrated and there are virtually no studies on devinylation. The potential of the vinyl group would also stimulate further research in this interesting area of chemistry.

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