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Alkenylphenols: preparation, transformations and applications

A M Maharramov, M R Bayramov, M A Agayeva, G M Mehdiyeva, I G Mamedov

Baku State University
ul. Khalilova 23, AZ-1148 Baku, Azerbaijan

Published data on the synthesis and chemical reactivity of alkenylphenols, mainly vinyl, propenyl and allyl derivatives, are considered. The transformations of these compounds involving various functional groups are discussed. Particular attention is given to cyclization reactions, reactions with dihaloalkanes, as well as reactions based on diallyl-containing bisphenols. The results of studies of hydrogen bonding in alkenylphenols and their derivatives are presented. Data on the key applications of compounds of this class are given.
The bibliography includes 173 references.

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I. Introduction

Alkenylphenols and their functional derivatives find use in the development of composites for microelectronics [1, 2] and as photoresists,[3] antioxidants,[4, 5] physiologically active substances,[6] thermoset copolymers [7, 8] and other materials with practically valuable properties. Alkenylphenols are often used as modifying comonomers in the synthesis of polymers.[9] For example, the introduction of minor amounts of these compounds into the growing polymer chains endows macromolecules with stability against light.[10] The simultaneous presence of several reactive groups — carbon–carbon multiple bond, OH group and the aromatic ring — in the alkenylphenol molecules accounts for diverse chemical reactivity of these compounds.

During the last 15 years, no survey articles devoted to the chemistry of alkenylphenols were published except for one review [11] dealing with the Claisen rearrangement of the allyl ethers of some classes of organic compounds. The present review summarizes the literature data and results of authors' studies carried out in this area. The most important methods for the synthesis and reactivity of alkenylphenols and the key applications of these derivatives are discussed.

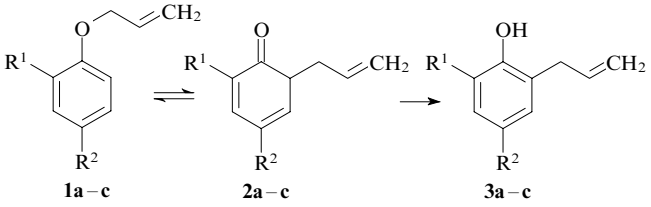
A M Maharramov Doctor of Chemical Sciences, Academician of the Azerbaijan Academy of Sciences, Chancellor of the BSU.
Telephone: +994(12)430 – 3245, e-mail: rector@bsu.az
M R Bayramov Doctor of Chemical Sciences, Professor, Head of the Chair of Oil Chemistry and Chemical Technology, Head of the Laboratory of Alkenylphenols at the BSU.
Telephone: +994(51)896 – 2300, e-mail: musa.bayramov@list.ru
M A Agayeva Candidate of Chemical Sciences, Leading Researcher at the same Laboratory.
Telephone: +994(55)966 – 4149
G M Mehdiyeva Candidate of Chemical Sciences, Researcher at the same Laboratory.
Telephone: +994(51)958 – 0604, e-mail: mehdiyeva_gm@mail.ru
I G Mamedov Doctor of Chemical Sciences, Professor at the Chair of Oil Chemistry and Chemical Technology at the BSU.
Telephone: +994(50)739 – 2131, e-mail: ib.nmrlab@list.ru
Current research interests of the authors: chemistry of alkenylphenols and heterocyclic compounds, metal corrosion inhibitors, sorption materials.

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II. Examples of the synthesis of allyl-, vinyl- and propenylphenlos and O-alkylated phenol derivatives

A well-known and widely practically utilized method for the synthesis of allylphenols is the thermal Claisen rearrangement of allylaryl ethers.[12 – 14] Although the mechanism of this reaction is considered to be known, there are some contradictions in interpretation of the pathway to final products. In order to elucidate the key pathways, Klyucharева *et al.*[15] performed quantum chemical calculations [B3PW91/6-31G(d) method and GAMESS program package]. For allylphenyl ethers **1a – c**, the authors calculated the possible reaction alternatives involving the intermediate formation of cyclohexadienones **2a – c** and yielding allylphenols **3a – c** (Scheme 1).

Scheme 1

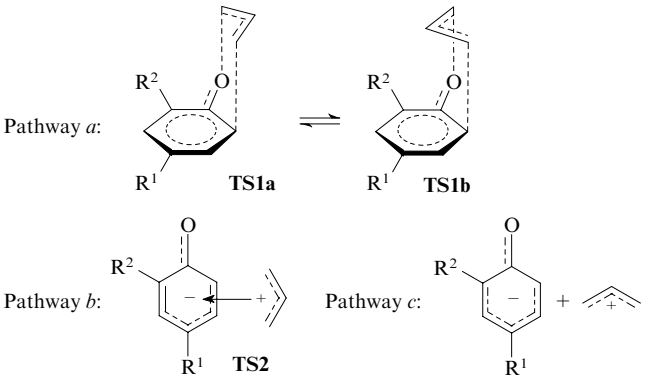


1a–c **2a–c** **3a–c**

R^1 = H: R^2 = H (**a**), Me (**b**); R^1 = Me, R^2 = H (**c**)

Three key pathways were considered, namely, intramolecular concerted [3,3]-sigmatropic shift giving transition states **TS1a** or **TS1b** (pathway *a*); the formation of intramolecular π-complex **TS2** followed by its rearrangement or allyl group migration (pathway *b*); and heterolysis of the ether bond to generate the allyl cation with subsequent C-alkenylation of the phenoxide anion (pathway *c*) (Scheme 2).

Scheme 2



According to calculations, the reaction by pathway *c* is unlikely. The intermediate dienones can be formed by pathways *a* and *b*, and this accounts for the formation of *ortho*- and *para*-substituted alkenylphenols. It was suggested that under conditions of the rearrangement, it is possible to obtain dialkenyl- and even trialkenylphenols (provided that the *ortho*- and *para*-positions of the aromatic ring are free).

The starting compounds **1a–c** can be prepared from allyl halides and phenols in the presence or in the absence of solvents.[14,16] The rearrangement of allyl ethers **1a**,**b** is carried out in some cases with convective or microwave heating.[17,18] In recent years, microwave activation has been preferred, because in this case, the rate constants for the rearrangement of these compounds increase 30- and 60-fold, respectively, compared with the convective heating.

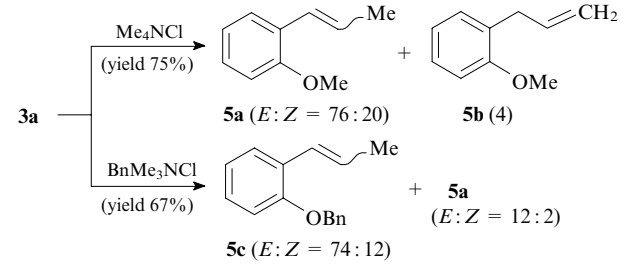
Wagholikar *et al.*[19] carried out the Claisen rearrangement of allyl phenyl ethers in the presence of β-zeolite, mordenite and type Y zeolite (with different Si : Al ratios). However, apart from compounds **3**, the reactions gave 2,3-dihydro-2-methylbenzofuran.

Unusual syntheses of alkyl aryl ethers using tetraalkylammonium salts in diglyme or polyethylene glycol (PEG) in the presence of NaOH at 150–160 °C have been reported.[20] Quaternary ammonium salts are used rather rarely as electrophilic reagents. In the authors' opinion, the first step of the reaction results in the formation of ion pairs, which then break up to give the alkylated hydroxy group. For example, for tetramethylammonium chloride, this mechanism is represented by reaction (1).

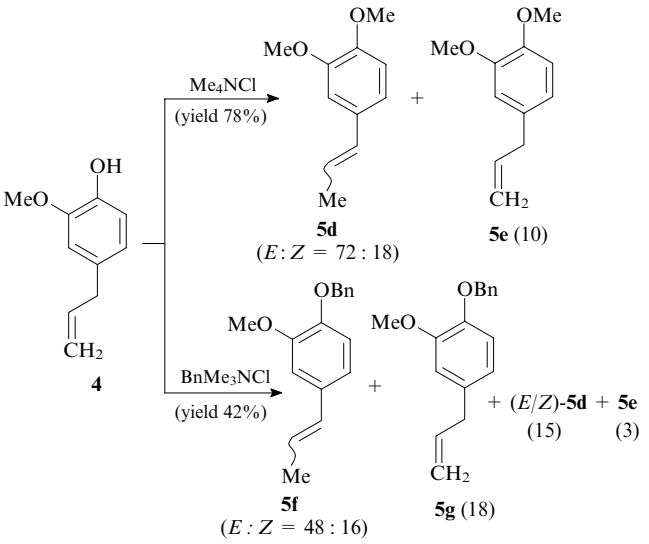
$$ArOH + Me_4NCl \longrightarrow [ArO^-Me_4N^+] \longrightarrow ArOMe + Me_3N \quad (1)$$

By reactions of 2-allylphenol (**3a**) and eugenol (**4**) with tetraalkylammonium salts in PEG, compounds **5a–g** were obtained in 4 h; mixtures of O-alkylated propenyl derivatives in which *E*-isomers predominated were formed as the major products. Also, alkylphenols with an unisomerized double bond were found as by-products, and in the case of benzyltrimethylammonium chloride, not only O-benzyl but also O-methyl derivatives were obtained (Schemes 3 and 4; the relative amounts of the products in the reaction mixture are given in parentheses).

Scheme 3



Scheme 4

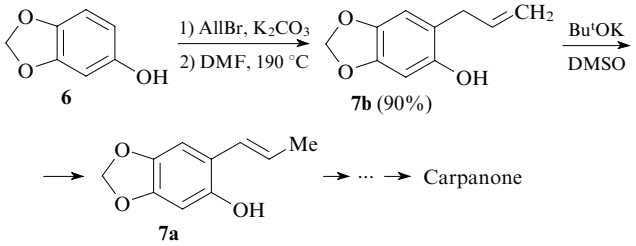


Allylphenol **3a**, which was found in the cornel flowers (*Cornus mas* L.),[21] was investigated[22–24] as an agent against some fungi (*Botrytis cinerea, Magnaporthe oryzae, Rhizoctonia cerealis* and *Alternaria solani*). When present in an amount of 800 mg kg^{-1}, this compound shows fungicidal activity and can protect tomato fruit and leaves as well as the seeds of the *Ginkgo biloba* L tree from microbial damage.

Phenol derivatives play a role in the development of effective plant-based antimalarial, antimicrobial and antihypertensive drugs. For example, sesamol (**6**) was used as the starting compound for the total synthesis of the natural lignane carpanone isolated from the carpano tree.[25]

The key step of the synthesis is the Suzuki–Miyaura cross-coupling reaction using propenyl derivative **7a** (Scheme 5).

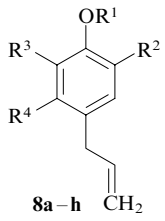
Scheme 5



The allyl group was introduced into sesamol by treatment with allyl bromide on heating in DMF; compound **7b** thus formed readily isomerized to propenylphenol **7a** under basic conditions.

Protti *et al.*[26] synthesized biologically active allylphenols and ethers **8a**–**h** by photochemical allylation of chlorophenols or chloroanisoles with allyltrtimethylsilane. The reaction was carried out in a polar solvent — acetonitrile or trifluoroethanol. Note that structurally related compounds were detected in *Piper* plants.

Structures 8



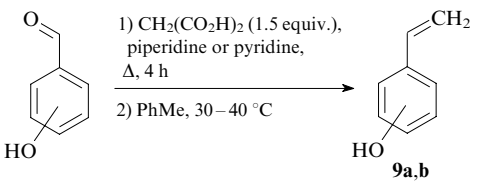
Compound **8**	R^1	R^2	R^3	R^4
a	H	H	H	H
b	H	OH	H	H
c	Me	OMe	H	H
d	H	OMe	H	H
e	Me	OAr	H	H
f	CH_2O		H	H
g	CH_2O		H	OMe
h	CH_2O		OMe	H

Estragole (4-allylanisole) was synthesized *via* this route in a moderate yield from the appropriate *p*-fluorophenyl derivative or diazonium salt. These photochemical transformations follow a fairly complex mechanism; the authors believe that arylcationic intermediates are formed.

Alkenylphenols containing a vinyl, propenyl or isopropenyl group in the aromatic ring are highly reactive, and, hence, they are used in polymerization.[27–32] A number of methods for the preparation of these derivatives have been developed.

A convenient method for the synthesis of vinylphenols **9a**,**b** is the condensation of hydroxybenzaldehyde with malonic acid in the presence of organic bases (Knoevenagel–Doebner reaction) followed by vacuum evaporation with toluene.[33] The reaction is accompanied by decarboxylation and gives 4-vinylphenols instead of the expected 4-hydroxycinnamic acids (Scheme 6).

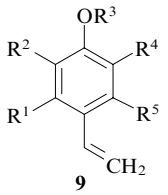
Scheme 6



Isomers: *ortho* (**a**, 38%), *para* (**b**, 86%)

Microwave initiation opened up new prospects for this process. A number of vinyl derivatives **9** were prepared by the reactions of ring-substituted phenols with malonic acid.[34]

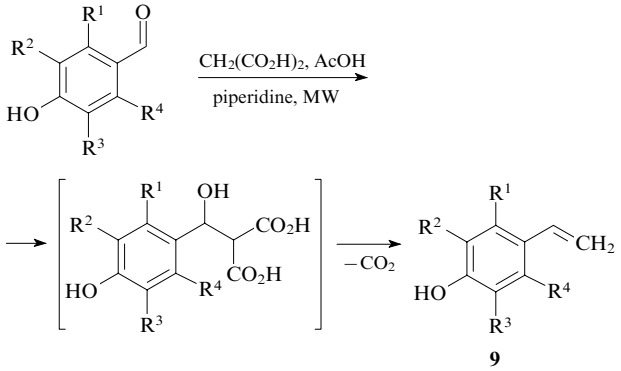
Structures 9



R^1, R^2, R^4, R^5 = H, OH, OMe;
R^3 = H, Me

A one-step synthesis of *p*-vinylphenols **9** containing various functional groups in the aromatic ring has been reported[35] (Scheme 7). This reaction is conducted in the presence of an acetic acid–piperidine mixture as the condensing reagent under focused microwave radiation. The authors proposed a mechanism for the reaction. The yields of vinyl derivatives reach 69% (the lowest yield of 7% was found for 3-methoxy-5-nitro-4-vinylphenol); for *ortho*- and *meta*-isomers, the corresponding cinnamic acids are the major reaction products under these conditions.

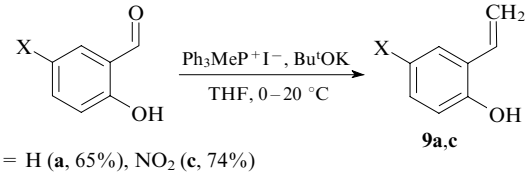
Scheme 7



R^1, R^2, R^3, R^4 = H, OH, OMe, Br, NO_2;
MW is microwave radiation

Elias *et al.*[36] obtained compounds **9a**,**c** by the Wittig reactions of salicylaldehyde and its nitro derivative with a quaternary phosphonium salt (Scheme 8).

Scheme 8



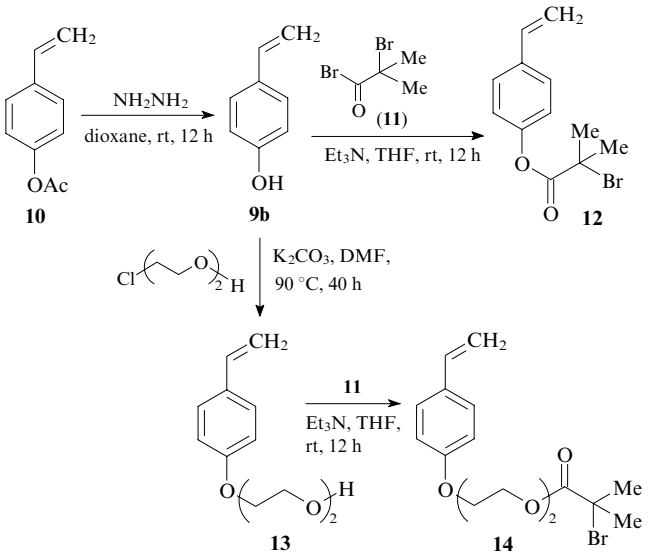
X = H (**a**, 65%), NO_2 (**c**, 74%)

Lately, enzymatic methods for preparation of organic compounds, including alkenylphenols, have received a lot of attention. For example, 4-vinylphenol (**9b**) is formed upon decarboxylation of *p*-coumaric acid in the presence of lactobacteria.[37] Alkenylphenol dimers were also prepared under the tandem action of laccases and lipases on isoeugenol (2-methoxy-4-propenylphenol) and 4-vinylguaiacol.[38]

Moine *et al.*[39] reported the synthesis of compound **9b** by the reaction of 4-acetoxystyrene (**10**) with hydrazine. The authors performed several transformations involving hydroxy groups in which the vinyl group is retained (Scheme 9). Reaction of vinylphenol **9b** with 2-bromo-2-methylpropionyl bromide (**11**) yielded 4-vinylphenyl

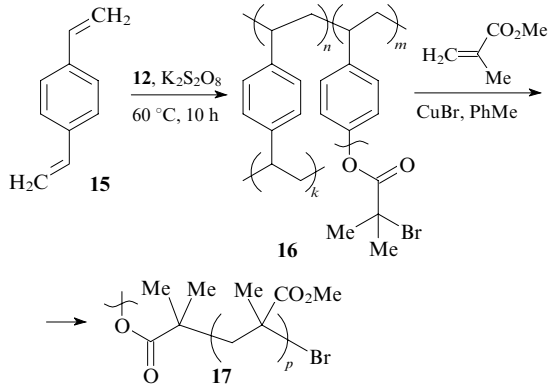
2-bromo-2-methylpropionate (**12**), while reaction with 5-chloro-3-oxapentanol gave 5-(4-vinylphenoxy)-3-oxapentan-1-ol (**13**). The latter was converted to 5-(4-vinylphenoxy)-3-oxapentyl 2-bromo-2-methylpropionate (**14**) in high yield (95%). Compounds **12** – **14** serve as promising substrates for polymerization reactions.

Scheme 9



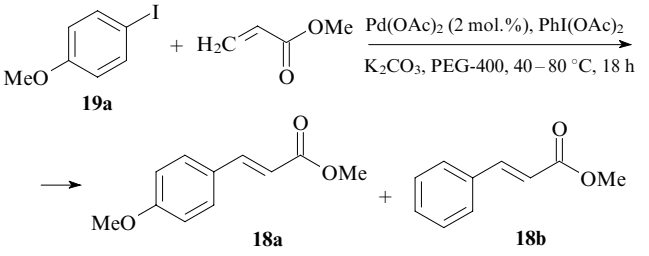
For example, emulsion copolymerization of monomer **12** with *p*-divinylbenzene (**15**) in the presence of potassium persulfate gave cross-linked copolymers **16** containing a bromine atom (Scheme 10).[39] Treatment of copolymers **16** with methyl methacrylate in the presence of the CuBr catalyst yielded modified cross-linked copolymers **17**.

Scheme 10



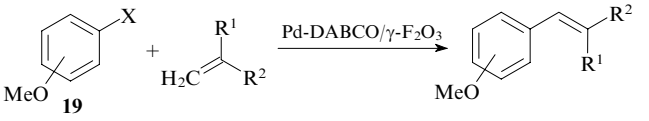
It is known[40] that the reaction of iodine-containing aromatic compounds with alkenes in the presence of palladium catalysts (Heck reaction) can serve to synthesize various alkenylaromatic compounds, and the product yields increase in the presence of hypervalent iodine compounds. Under these conditions, the authors were able to prepare alkenylanisole **18a** from iodoanisole (**19a**) and methyl acrylate. However, in the absence of di(acetoxy)iodobenzene, compound **18a** was formed in 42% yield, while in its presence, the yield was 18%. In the latter case, methyl cinnamate (**18b**) was the major product (Scheme 11).

Scheme 11



Under the action of the palladium complex with 1,4-diazabicyclo[2.2.2]octane (DABCO) supported on magnetic nanoparticles, haloanisoles **19** also react to form a new C – C bond with various alkenes without a solvent (a sort of Mizoroki – Heck reaction) (Scheme 12).[41]

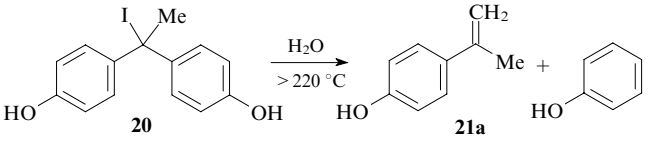
Scheme 12



X = I, Br, Cl; R^1 = H, Me; R^2 = Ph, CO_2Alk (Alk = Me, Et, Bu^n)

Cracking of bis-phenol **20** is the main method for the synthesis of *p*-isopropenylphenol (**21a**).[42] The reaction is carried out at a temperature of 220 – 240 °C in the presence of alkaline catalysts. It is noteworthy that undesirable side products — dimers and trimers — are also formed under these conditions. In order to increase the selectivity and suppress the side reactions, cracking is conducted in water under elevated pressure without any catalysts (Scheme 13).[43]

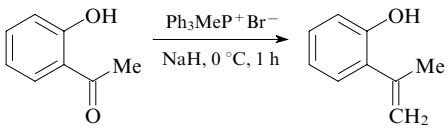
Scheme 13



The reaction gives only compound **21a** and phenol, which are easily separated by vacuum distillation.

o-Isopropenylphenol (**21b**) was obtained in high yield from 2-hydroxyacetophenone by the Wittig reaction (Scheme 14).[44]

Scheme 14

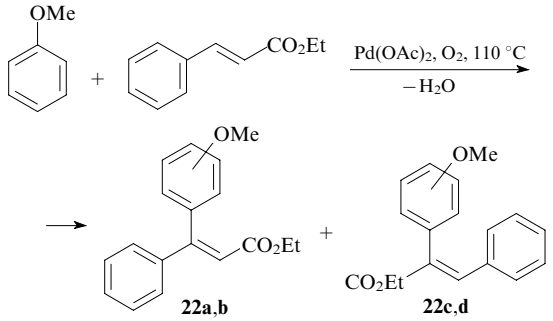


21b (90%)

Methyl ethers of alkenylphenols **22a** – **d** were synthesized by heterogeneous oxidative alkenylation of anisole with ethyl cinnamate catalyzed by an immobilized palladium catalyst in the presence of atmospheric oxygen (Scheme 15).[45] Under these conditions, the reaction affords a mixture of products with different positions of the internal double bond and different types of substitution in the benzene ring. The reaction mainly involves the β-position of the cinnamic acid, with *para*- and *ortho*-substituted

anisoles predominating. The major product — ethyl 3-(4-methoxyphenyl)-3-phenylpropanoate (**22a**) — was obtained in 45% yield, while *ortho*-isomer **22b** formed in 25% yield. Compounds **22c**,**d** were isolated in trace amounts. The selectivity of the reaction barely depends on the conditions, in particular, on the oxygen pressure. When the reaction proceeds at high temperature, a minor amount of the *meta*-isomer is also formed.

Scheme 15



Isomers: *para* (**a**, **c**) *ortho* (**b**, **d**)

III. Sulfur-, nitrogen- and phosphorus-containing alkenylphenols

Derivatives of phenols containing heteroatoms (S, N, P) in the molecule occupy a prominent place among polyfunctional compounds used as antioxidants for polymers or fuels and lubricants and as oxidation inhibitors for bioorganic substrates.[46–52] Below we describe synthesis of these compounds based on alkenylphenols.

III.1. Sulfur-containing phenol derivatives

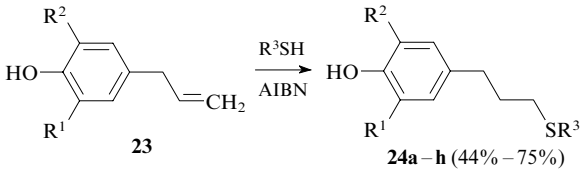
A convenient method for the synthesis of sulfur-containing phenols is homolytic addition of alkane- and arenethiols to a C=C bond of alkenes (thiylation reaction).[53] Using various alkenylphenols, sulfur-containing phenols [46, 54, 55] that possess valuable properties or can serve as the starting compounds for further transformations were obtained. For example, bis[3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl] sulfide is a high-performance heat stabilizer for polymer materials, mineral oils and edible fats and has a pronounced protective action in *in vivo* experiments on pathological states associated with activation of lipid peroxidation. High antioxidant activity was found for bis[3-(4-hydroxyaryl)propyl] sulfides [51] and alkyl 3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)propyl sulfides.[56]

The reactions of alkane- and arenethiols with alkenes are known to follow a homolytic mechanism when sources of free radicals (azo compounds or peroxides) are present and on exposure to UV radiation or light.[57, 58] In the presence of radical acceptors (*e.g.*, piperidine) or in the dark, these processes are much slower.

The synthesis of sulfur-containing phenols has been described in numerous papers.[46, 51, 56, 59–62] For example, 2,6-dialkyl-4-allylphenols **23** and alkanethiols were converted in the presence of azobis(isobutyronitrile) (AIBN) to 4-[3-(alkylsulfanyl)propyl]phenols **24a**–**h** in good yields (Scheme 16).[46]

Compounds **24a**–**f** with *ortho*-methyl and -cyclohexyl substituents proved to be high-performance oxidation inhibitors for mineral oils and polymers.[46]

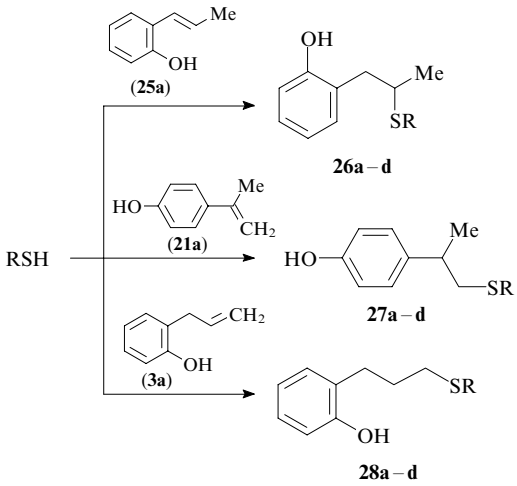
Scheme 16



Compound **24**	R^1	R^2	R^3
a	cyclo-C_6H_{11}	Me	Bu^n
b	cyclo-C_6H_{11}	cyclo-C_6H_{11}	Bu^n
c	cyclo-C_6H_{11}	cyclo-C_6H_{11}	n-$C_{12}H_{25}$
d	Me	Me	Bu^n
e	Me	Me	n-$C_{12}H_{25}$
f	Me	Me	n-$C_{18}H_{37}$
g	Bu^t	Bu^t	Bu^n
h	Bu^t	Bu^t	n-$C_{12}H_{25}$

As noted above, reactions of alkenylphenols with alkanethiols in the presence of initiators, induced by heat or UV light occur by a free radical mechanism. The reactions have high regioselectivity: thiyl radicals add to the β-carbon atom of the vinyl group (against the Markovnikov rule). Using this method, 2-(prop-2-enyl)- (**25a**), 4-isopropenyl- (**21a**) and 2-allylphenols (**3a**) were converted to disulfides **26**–**28** (Scheme 17).[57, 58, 63–65]

Scheme 17



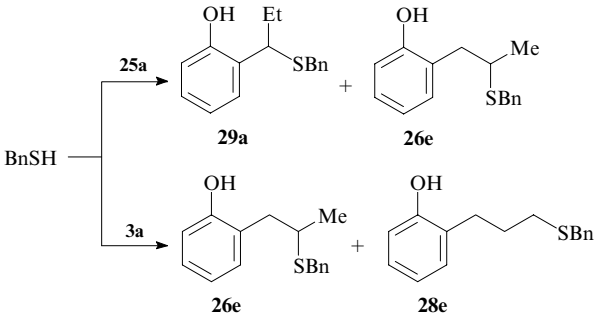
R = Et (**a**), n-C_5H_{11} (**b**), n-C_8H_{17} (**c**), n-$C_{12}H_{25}$ (**d**)

The thiylation of alkenylphenols depends considerably on the starting thiol structure. The dissociation energies (E_D) of S–H and S–C bonds in thiols are fairly high, being 318.8–448.5 and 238.1–355.2 kJ mol^{-1}, respectively. However, these bonds are weaker than the O–H and C–O bonds in alcohols (E_D = 337.0–437.6 and 373.2–405.8 kJ mol^{-1}). In the series of aliphatic thiols, the S–H bond energy tends to increase and the C–S bond energy tends to decrease as the alkyl chain length increases.[66] In the aromatic thiols, the S–H bond energy becomes lower, while the C–S bond energy is higher owing to p,π-conjugation, which is reflected in the yields of the final products.[65]

Alkenylphenol **25a** reacts with α-sulfanyltoluene giving rise to a mixture of isomeric 2-[1-(benzylsulfanyl)propyl]- (**29a**) and 2-[2-(benzylsulfanyl)propyl]phenols (**26e**) in 4 : 1

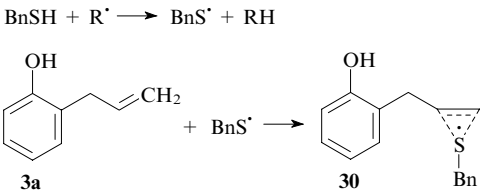
mass ratio (Scheme 18). A similar mixture of isomers **26e** and **28e** was obtained from 2-allylphenol (**3a**).[63]

Scheme 18



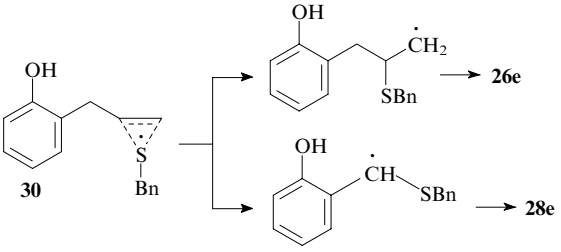
The presence of isomers is apparently caused by the formation of intermediate unstable thiirane radical **30** [Scheme 19; the example for 2-allylphenol (**3a**) is given; R designates any free radical generated from the initiator].

Scheme 19



Further transformations of radical **30** furnish the radical species that serve as sources of products **26e** and **28e** (Scheme 20). Compound **26e** is formed according to the Markovnikov rule, while the formation of regioisomer **28e** is attributable to the Kharasch effect.

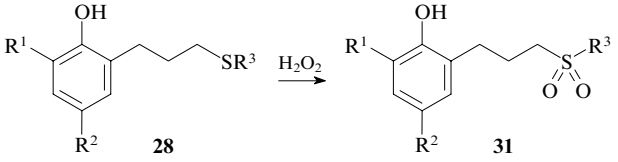
Scheme 20



The phenolic hydroxyl retards the thiylation of the alkenylphenols, the yield of the corresponding sulfides being not higher than 70%–75%. The thiylation of O-alkylated phenols affords the sulfides in high yields (up to 96%).

Compounds **28** were oxidized to sulfones **31** with hydrogen peroxide (Scheme 21).[67] The corresponding sulfoxides can also be obtained by partial oxidation of sulfides.

Scheme 21

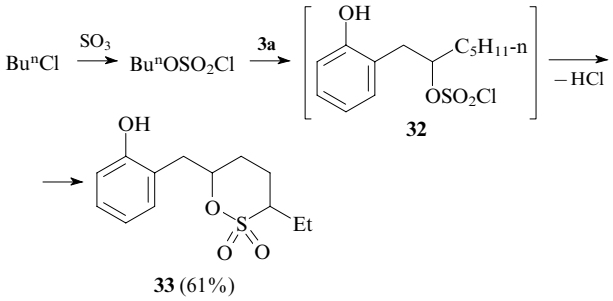


R^1, R^2 = H, Me; R^3 = n-C_5H_{11}, n-C_9H_{19}

Sulfur-containing phenols were also prepared by addition of various electrophilic reagents to alkenylphenols.[68] It was shown [69] that the electrophilicity of the reagents can be increased by activating them with sulfur trioxide, which is inserted into the carbon–heteroatom single bond. This results in generation of highly electrophilic intermediates able to easily add to unsaturated compounds.

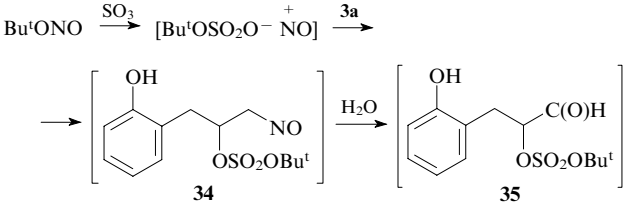
For example, the reaction of alkenylphenol **3a** with n-butyl chloride activated with sulfur trioxide proceeds *via* intermediate **32**, which undergoes intramolecular cyclization yielding 4-(2-hydroxybenzyl)-1-ethylbutane-1,4-sultone (**33**) (Scheme 22).[68]

Scheme 22



The reaction of compound **3a** with butyl nitrite activated with sulfur trioxide leads to sulfur-containing phenol **34**. This product is hydrolyzed being converted to compound **35** (Scheme 23).[70]

Scheme 23



III.2. Nitrogen-containing phenol derivatives

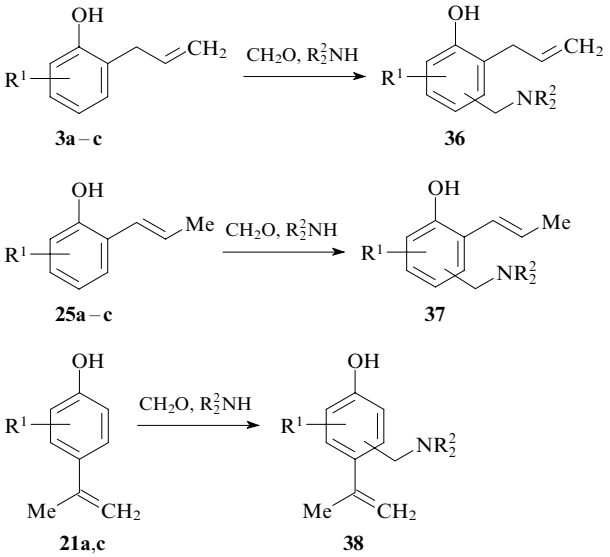
Among the methods used to prepare nitrogen-containing phenols, an important position is held by the ternary condensation involving 2-alkenylphenols **3a–c**, **21a**,**c** or 4-isopropenylphenols **25a–c**, formaldehyde and secondary amines (Mannich reaction) (Scheme 24). This process affords dialkylaminomethyl derivatives **36–38** in 45% to 88% yields.[49,71–73]

As regards the mechanism, this reaction is similar to the Knoevenagel condensation involving particularly the iminium intermediates. The electrophilic attack is performed by the iminium ion formed from amine and formaldehyde. In the case of 2-allylphenols **3a**,**b**, the dialkylaminomethyl group enters only the *ortho*-position, and if it is occupied (compound **3c**), then the *para*-position. The yields of aminomethylated derivatives are considerably affected by the nature of alkenylphenol and amine used.

For example, for allylphenols **3**, the highest yield (~71%) is observed for 2-allyl-6-(morpholinomethyl)phenol.

Nitrogen-containing alkenylphenols were also synthesized using other reagents — methylenebis(amines) and alkoxymethyl- and bis(alkoxymethyl)amines — in an anhydrous medium.

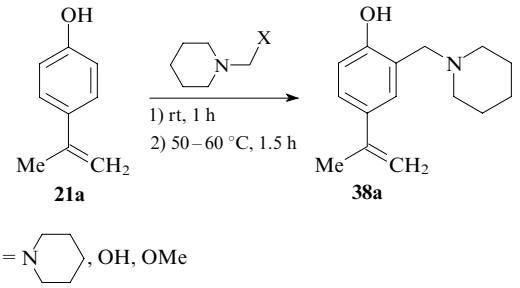
Scheme 24



3: R^1 = H (**a**), 4-Me (**b**), 6-Me (**c**); **21**: R^1 = H (**a**), 2-Me (**c**); **25**: R^1 = H (**a**), 4-Me (**b**), 6-Me (**c**); R^2 = Me, Et; $R^2 - R^2$ = $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

The reactions of 4-isopropenylphenol (**21a**) with methylenebis(piperidine) or with *N*-methoxy- and *N*-hydroxymethylpiperidines furnish 4-isopropenyl-2-piperidinomethylphenol (**38a**) (Scheme 25).[74] The hydroxy derivative is most reactive, while for methylenebis(piperidine) longer reaction times are required (2 days).

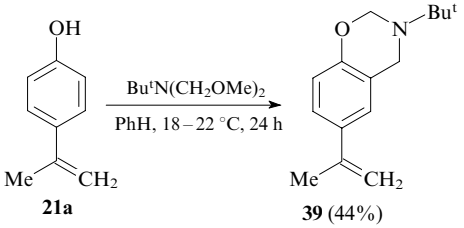
Scheme 25



X = N, OH, OMe

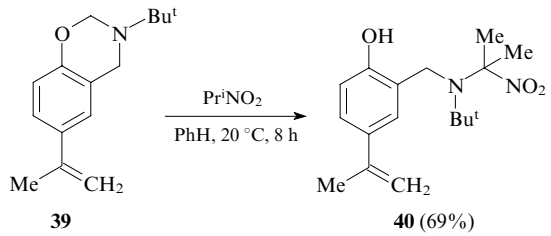
The reactions of alkenylphenols with functionally substituted amines can be accompanied by cyclization. A mixture of 4-isopropenylphenol (**21a**) with *tert*-butylbis(methoxymethyl)amine is converted to 3-*tert*-butyl-6-isopropenyl-3,4-dihydrobenz-1,3-oxazine (**39**) when kept in anhydrous benzene at 18–22 °C for 24 h (Scheme 26).[74]

Scheme 26



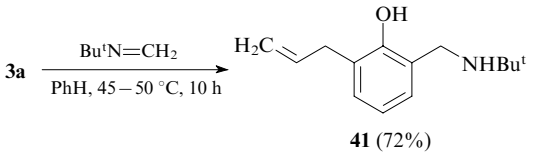
The reaction of compound **39** with 2-nitropropane is accompanied by heterocyclic ring opening giving phenol derivative **40** (Scheme 27).

Scheme 27



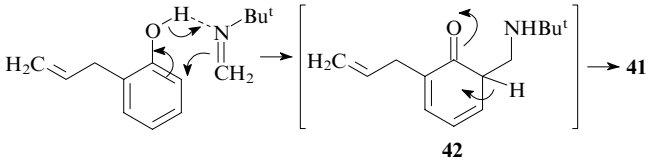
Heating 2-allylphenol (**3a**) with *tert*-butylmethyleneimine in benzene for 10–12 h affords compound **41** in a good yield (Scheme 28).[74]

Scheme 28



The predominant *ortho*-aminomethylation is attributable in this case to the formation of intermediate oriented π-complex **42** (Scheme 29).

Scheme 29

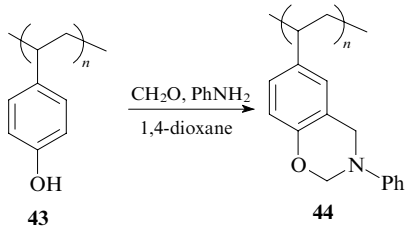


Currently the proportion of polymers obtained by radical polymerization is more than a half of the world output. Numerous problems related to the control of particular stages of polymer synthesis and the molecular-mass distribution stimulated the search for entirely new approaches to addressing them.[75] A concept of controlled synthesis of macromolecules under radical inhibition conditions in the presence of nitroxides such as 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) has been developed.[76]

The synthesis of high-molecular-mass copolymers by radical copolymerization can also be approached in a different way. The presence of intramolecular or intermolecular hydrogen bond in polymers and copolymers obtained from aminomethyl derivatives of alkenylphenols affects to one or another extent their physicochemical and functional properties. This is especially important for the problem of provision of polymeric materials with long-lasting heat and light stability.[9] The presence of such stable intramolecular hydrogen bond in *ortho*-aminomethylated alkenylphenols makes it possible to eliminate the inhibiting effect of the phenolic hydroxyl on the polymer chain growth and thus to synthesize high-molecular-mass copolymers with styrene (or other vinyl comonomers), which exhibit good antioxidant properties.

The aminomethyl group can also be introduced into the phenol aromatic ring *via* polymer-analogous reactions, *e.g.*, using alkenylphenol polymers **43** (Scheme 30).[42,77]

Scheme 30



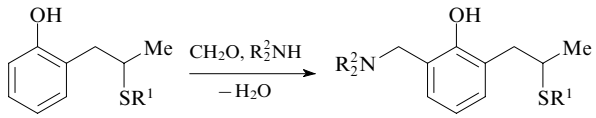
43 **44**

The reaction of polymer **43** with formaldehyde and aniline was found to give polymer **44** containing benzoxazine moieties.

III.3. Phenols containing both nitrogen and sulfur atoms

A convenient method for the synthesis of phenols containing both nitrogen and sulfur atoms in substituents is aminomethylation of compounds **26a**,**b** [R^1 = Et (**a**), n-C_5H_{11} (**b**)] (Scheme 31).[55, 78, 79]

Scheme 31

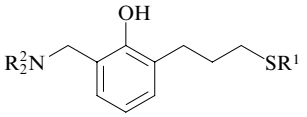


26a,**b** **45**

R^1 = Et, n-C_5H_{11}; R^2 = Me, Et; $R^2–R^2$ = $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

A similar condensation with formaldehyde and secondary amines carried out for the products of thiylation of allylphenols **3** furnishes compounds **46**.[54, 80]

Structures 46



46

R^1 = n-C_5H_{11}, n-C_9H_{19}, n-$C_{12}H_{25}$; R^2_2N = Me_2N, Et_2N, cyclo-$O(CH_2CH_2)_2N$, cyclo-$(CH_2)_5N$

Sulfur- and nitrogen-containing propenylphenols can serve as antioxidants. They are effective combined action inhibitors, participating in chain termination by peroxide radicals and in hydroperoxide decomposition.[55] Alkenylphenol derivatives of this type exhibit complexing properties towards palladium(II) ions,[54] which is important for the development of new catalysts. Testing of these compounds as inhibitors of metal corrosion in hydrocarbon and aqueous salt solutions saturated with hydrogen sulfide and as antimicrobial oil and fuel additives demonstrated that they can be used in various materials to improve antioxidant and antimicrobial properties and corrosion resistance.[71–73, 78]

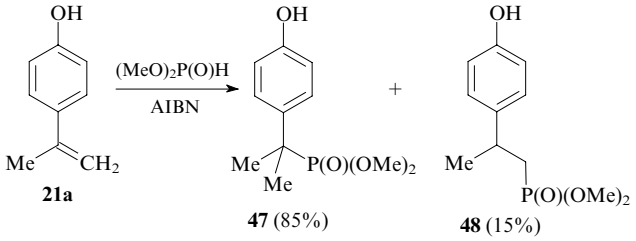
Quaternary ammonium salts obtained from allyl- and propenylphenols *via* successive thiylation, aminomethylation and quaternization reactions proved to be good antimicrobial additives.[81]

III.4. Phosphorus-containing phenols

A classical method for the preparation of organophosphorus compounds is the addition of dialkyl phosphites to multiple bonds (Pudovik reaction).[82, 83] Alkenylphenols are suitable as substrates for this reaction.

Maharramov *et al.*[50] investigated reactions of alkenylphenols with dialkyl phosphites under various conditions (in the presence of free radical initiators, on heating and on exposure to UV radiation) and proposed the key pathways to the final products. For example, 4-isopropenylphenol (**21a**) reacts with dimethyl phosphite in the presence of the initiator (AIBN). The major product is 4-[1-methyl-1-(dimethoxyphosphoryl)ethyl]phenol (**47**), while 4-[1-methyl-2-(dimethoxyphosphoryl)ethyl]phenol (**48**) was isolated as a minor product (Scheme 32).

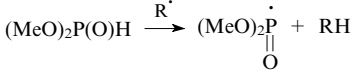
Scheme 32



21a **47** (85%) **48** (15%)

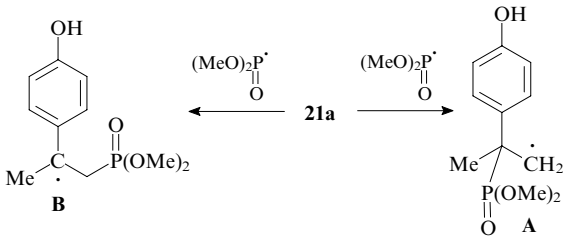
In the authors' opinion, the phosphorylation of compound **21a** involves dimethylphosphoryl radicals generated by the action of initiator-derived radicals (R$^\bullet$) (Scheme 33).

Scheme 33



The formation of two types of phosphorus-containing radicals is possible, namely, primary (**A**) and tertiary ones (**B**) (Scheme 34).

Scheme 34



B **A**

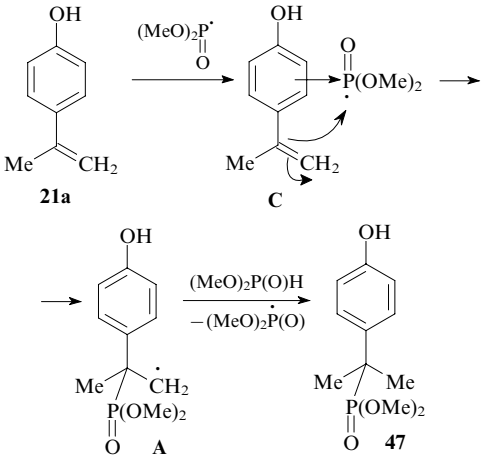
Subsequently radicals **A** and **B** react with dimethyl phosphite, which results in the formation of products **47** and **48** and liberation of the dimethylphosphoryl radical.

This behaviour of dimethyl phosphite towards alkenyl phenol can also be explained in a different way:[84] first, donor–acceptor π-complex **C** is formed as a result of interaction of the benzene π-electrons of compound **21a** with vacant d-orbitals of phosphorus (Scheme 35). With the participation of the double-bond π-electrons of the isopropenyl group, this complex is converted to radical **A**. In the last step, radical **A** attacks the dimethyl phosphite molecule and phosphorus-containing phenol derivative **47** is formed as the final product according to the Markovnikov rule.

It was shown by ^{1}H NMR spectroscopy that phosphorylation involves intermediate formation of complex **C**. This can also be detected by the colour change of the reaction mixture: as compound **21a** is added to dimethyl phosphite, the solution immediately acquires a pale pink colour.[84]

In the reaction of dimethyl phosphite with O-alkylated 4-isopropenylphenol, the key regular patterns of the addition of dimethyl phosphite to a double bond are retained,[85]

Scheme 35

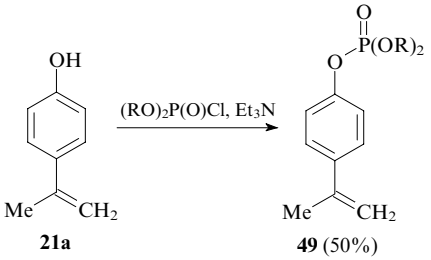


but the overall yield of phosphorylation products decreases to 78%. This implies a beneficial effect of the phenolic hydroxyl on the course of homolytic addition of dialkyl phosphites to multiple bonds.

When alkenylphenol **21a** is phosphorylated under thermal conditions (on heating to 130 °C), the addition also mainly obeys the Markovnikov rule but the yield of the major product is much lower (~30%).[50]

The reaction of compound **21a** with chlorophosphites in the presence of triethylamine leads to phosphorus-containing esters **49** (Scheme 36).[42]

Scheme 36



R = Me, Et

IV. Hydrogen bonds in alkenylphenols and their derivatives

Studies of intramolecular and intermolecular interactions in nitrogen-containing phenols, alkenylphenols and copolymers involving them receive much attention in the literature.[86–89] The behaviour of these compounds in solutions is considerably affected by the position of the amine group relative to the OH group enabling the formation of a stable O – HN bond.

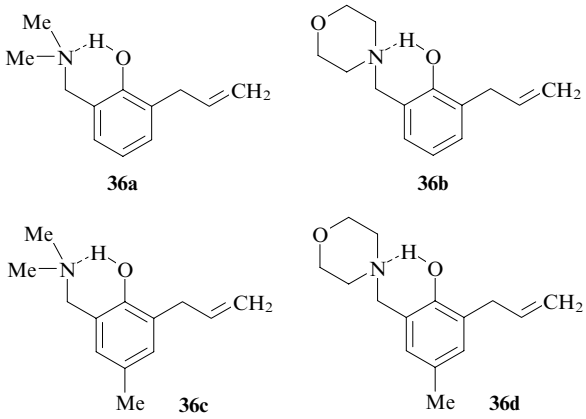
The formation of an intramolecular hydrogen bond in 2-amino-4,6-di-*tert*-butylphenol was revealed by FT IR spectroscopy; this bond influences the reactivity of this compound in solutions and its antiviral activity.[86]

Berdyshev *et al.*[90] reported the results of conformational analysis and the data of IR spectra for various substituted *o*-allylphenols. The quantum chemical B3LYP/6-31G method was used to construct two-dimensional cyclic potential energy surfaces for the internal rotation of the allyl substituent and its vinyl group depending on the OH group orientation. It was shown that compound **3a** exists in the gas phase as a mixture of eight non-planar rotamers and eight optical isomers. However, the possibility of formation of OH···π-electron type intramolecular hydrogen bonds in the gas phase was established only for four rotamers.

Bayramov and co-workers[91,92] studied the molecular dynamics of compounds **36** in solution (in CCl_4) by ^1H and ^{13}C NMR spectroscopy. In the ^1H NMR spectra of compounds **36a – d**, the signals of the hydroxy group were observed at 10.12, 10.04, 9.43 and 9.37 ppm, respectively, while in the spectra of the starting alkenylphenols, they occurred at 4.8 – 6.5 ppm. This attests to the formation of a fairly strong intramolecular hydrogen bond in these compounds.

In the case of 2-allyl-6-(*tert*-butylaminomethyl)phenol, no intramolecular hydrogen bond was found, which is attributable to steric hindrance created by the bulky *tert*-butyl substituent in the aromatic ring.

Structures 36a – d

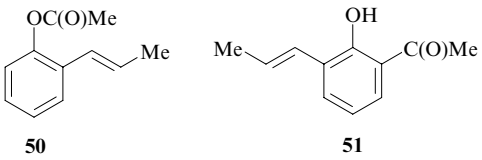


An intramolecular hydrogen bond is also detected in some compounds containing N and S atoms, for example, in 2-dimethylaminomethyl-6-(3-n-pentylsulfanylpropyl)phenol (**46a**; R^1 = n-C_5H_{11}, R^2 = Me).

Of certain interest is also the study of molecular dynamics of phenol acetates and their alkenyl derivatives.[93] The reason is that the carbonyl-containing alkenylphenols are widely used in organic synthesis and as monomer stabilizers in the preparation of polymeric materials stable against light and heat. Using the procedure reported by Bakhmutov,[94] the values of ^1H and ^{13}C spin–lattice relaxation were calculated. In addition, the authors determined the activation energy for the molecular motions of some phenolic compounds in 5% and 10% solutions in acetone-d_6.

To study the molecular dynamics of alkenyl phenols **50** and **51**, calculations for model compounds: phenyl acetate, *p*-tolyl acetate and their derivatives — 2-hydroxyacetophenone and 2-hydroxy-5-methylacetophenone — were first carried out.

Structures 50, 51



For the methyl groups of these compounds, ^1H and ^{13}C spin – lattice relaxation times (T_1) were calculated at various temperatures and various concentrations in solution (in acetone-d_6). The results showed that out of the possible

relaxation mechanisms, the C—H dipole–dipole coupling prevails for these moieties.

The activation energies for molecular motion were determined from the temperature dependence of the spin–lattice relaxation caused by dipole–dipole coupling. The difference between the activation energies of the molecular motion for methyl groups for ^{1}H and ^{13}C nuclei provided the conclusion that they undergo anisotropic molecular reorientation in the liquid.[94]

For compound **50**, T_1 were found to be close to those for aromatic hydrocarbons, which contain hydrogen atoms; this is attributable to the absence of a predominant rotation axis in this molecule. Comparison of the relaxation times of two CH_3 groups and CH group demonstrated that the time T_1 for the CH_3-group carbon is longer than that for the CH-group carbon. The results indicate that apart from the dipole–dipole (DD) relaxation of the methyl groups, spin–rotation (SR) relaxation takes place. For the carbon atoms of the carbonyl and propenyl CH_3 groups, the contributions of the DD and SR relaxations are related as 94 : 6 and 87.5 : 12.5, respectively.

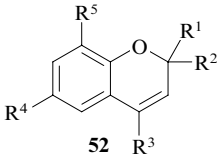
As regards the behaviour of 2-hydroxy-3-propenylacetophenone **51**, the results of calculations also point to its relatively anisotropic molecular reorientation in the liquid. A study of hydrogen bonding in this compound (as 5% solutions in acetone-d_6 and CCl_4) showed that in tetrachloromethane, the signal of the hydroxy group occurs at 12.74 ppm. Upon interaction with acetone-d_6, the signal of the hydroxy group shifts to 12.93 ppm, which is indicative of the formation of only an intramolecular hydrogen bond in the polar solvent.

V. Cyclization

In the last 10–15 years, alkenylphenols have attracted researchers' attention owing to the extensive opportunities for converting them to carbo- and heterocyclic compounds.

For instance, one method for the synthesis of 2*H*-1-benzopyran (chromene) derivatives **52** is cyclization of allylphenols in the presence of palladium catalysts.[95]

Structures 52



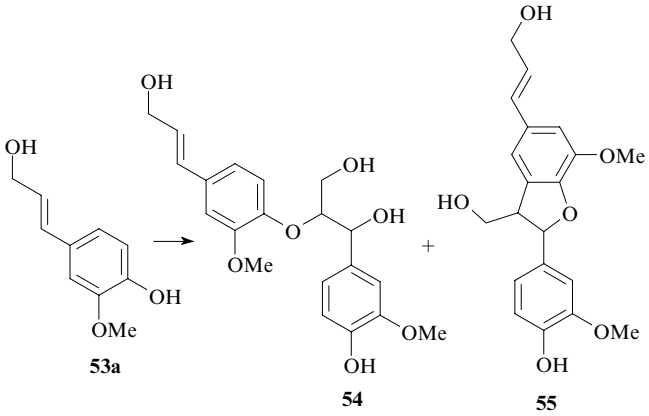
52

R^1, R^3 = H, Me, Ph;
R^2, R^5 = H, Me;
R^4 = H, OMe, Ac, CN

The reaction occurs in a DMSO–water mixture (9 : 1) at 60 °C in the presence of air. It was found that when electron-withdrawing substituents are present in the *para*-position of the aromatic ring of allylphenol, the yields of the corresponding benzopyrans **52** decrease.

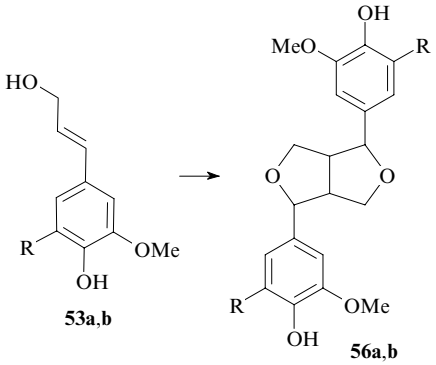
Syrjanen and Brunov[96] described regioselective enzymatic oxidation of coniferyl alcohol (**53a**) and its analogues **53b**,**c**, which have a double bond conjugated with a benzene ring. Depending on the structure of the starting compounds, oxidative cross-coupling [H_2O_2, HRP (horseradish peroxidase), Me_2CO, H_2O] gives different dimeric compounds **54**–**58** (Scheme 37–39). In all cases, phenols **53** are coupled at the β-position. No yields or product ratios are presented in the original publication.

Scheme 37



53a **54** **55**

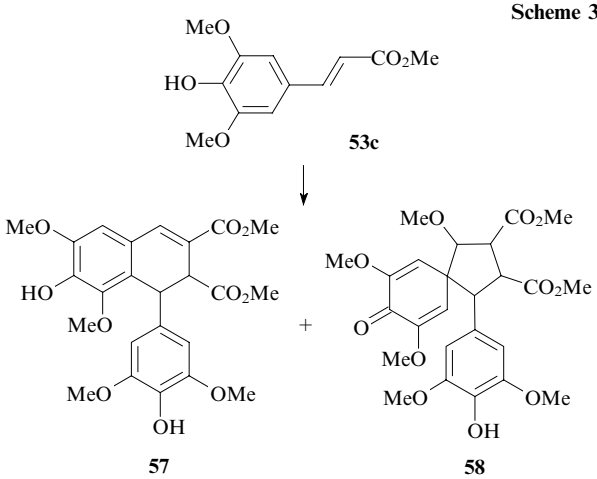
Scheme 38



53a,**b** **56a**,**b**

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

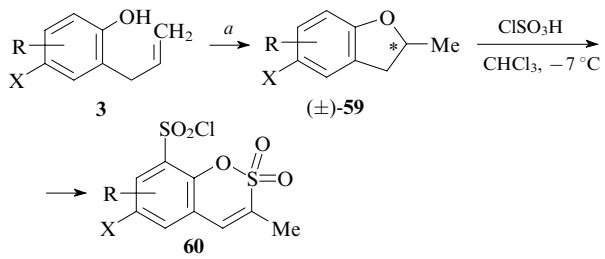
Scheme 39



53c **57** **58**

Qaisi *et al.*[97] carried out one-pot intramolecular cyclization of allylphenols **3** containing various substituents in the aromatic ring. 2-Methyl-2,3-dihydrobenzofurans **59** thus formed were treated with chlorosulfonic acid at −7 °C to give the corresponding cyclic sulfonates (sultones): 8-chlorosulfonyl-1,2-benzoxathiine 2,2-dioxides **60**. These compounds can be used as intermediates for the synthesis of herbicides and plant growth regulators derived from sulfonylureas (Scheme 40).

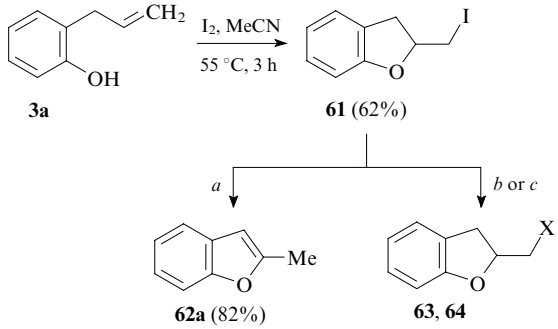
Scheme 40



X = Cl, Br; R = H, Hal, NO_2, CN, C(O)Alk, OR′, SR′ (R′ = Alk, alkenyl, alkynyl);
(*a*) 1) $Hg(OAc)_2$, THF, Δ; 2) $NaBH_4$, NaOH (aq.);
3) KOH (aq.), Δ; then HCl (aq.), 0 °C

Merzlov *et al.*[98] cyclized compound **3a** in the presence of molecular iodine (iodocyclization). The reaction proceeded in acetonitrile on gentle heating without a catalyst and gave 2-iodomethyl-2,3-dihydrobenzofuran (**61**). The authors studied the reaction by gas chromatography–mass spectrometry and elucidated the conditions for the formation of cyclization product **61** in good yield and with a high degree of purity.[99] On heating in the presence of bases, compound **61** is converted to 2-methylbenzofuran (**62a**), and displacement of iodine by O- and N-nucleophiles furnishes new benzofuran derivatives **63** and **64** (Scheme 41).

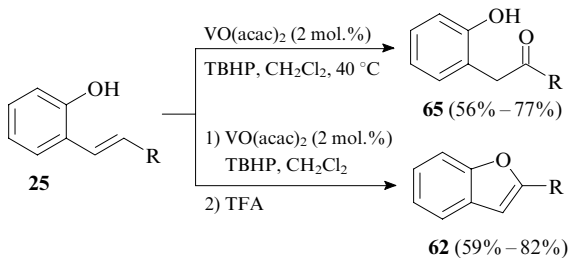
Scheme 41



X = OAc (**63**), NR^1R^2 (**64**) ($R^1–R^2 = (CH_2)_5$, $(CH_2)_2O(CH_2)_2$; R^1 = H, $R^2 = C_6H_4Me$-4);
(*a*) KOH, AlkOH, Δ or K_2CO_3, DMSO, Δ;
(*b*) for X = OAc: AgOAc (2.5 equiv.), MeCN, Δ, 2 days (32%) or NaOAc (2.5 equiv.), DMF, Δ, 2 days (66%);
(*c*) for X = NR^1R^2: R^1R^2NH (2.5 equiv.), 20 °C or DMF, 70 °C

Lattanzi *et al.*[100] described the oxidation of *o*-alkenylphenols **25** with *tert*-butyl hydroperoxide (TBHP) catalyzed by $VO(acac)_2$ (acac is acetylacetonate) (Scheme 42). Depending on the conditions, the reaction gave *o*-hydroxybenzyl ketones **65** or benzo[*b*]furans **62**.

Scheme 42

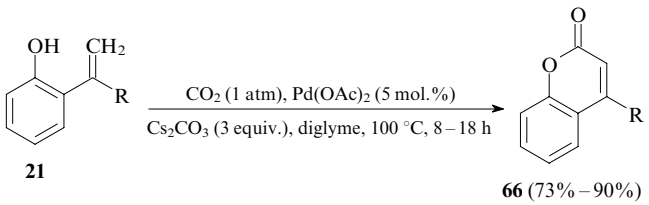


R = Me, Bu^n, Bu^s, Bu^t, Ph;
TFA is trifluoroacetic acid

The formation of compounds **65** was interpreted as resulting from rearrangement of the intermediate epoxyphenols. When trifluoroacetic acid is added, selective cleavage of the benzyl C–O bond and 1,2-migration of the hydride ion take place, yielding only products **62**.

Data concerning the synthesis of coumarins **66** by carboxylation of compounds **21** in the presence of $Pd(OAc)_2$ and Cs_2CO_3 were reported [101] (Scheme 43).

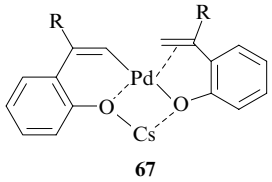
Scheme 43



R = H, Me, XC_6H_4 (X = H, 4-OMe, 2-Me, 4-CF_3, 4-CN, 4-Br)

In the authors' opinion, this reaction involves the formation of alkenyl palladium intermediate **67**, the content of which in the reaction mixture is 74% for R = Ph (^{1}H NMR data).

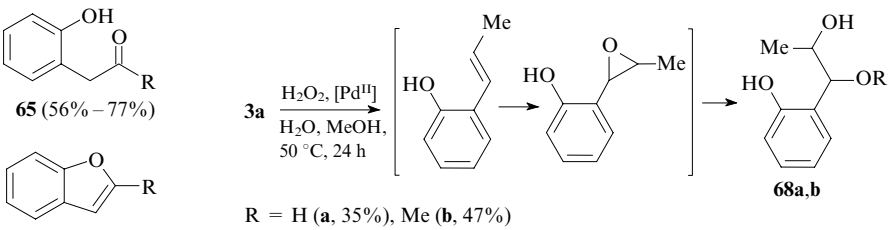
Structure 70



Since coumarin and its derivatives, which are abundant in nature, possess high biological activities, of interest is the development of new methods for the synthesis of these derivatives. The reaction presented above differs substantially from the known Pechmann method for coumarin synthesis (see, for example, Ref. 102) and extends the range of accessible compounds of this class that cannot be synthesized by other methods.

Thiery *et al.*[103] described the oxidation of compound **3a** with hydrogen peroxide in aqueous methanol in the presence of a Pd catalyst — a $Pd(OC(O)CF_3)_2$–$[(HOCH_2CH_2NHC(O)CH_2)_2NCH_2]_2$ system. This reaction affords a mixture of *syn*- and *anti*-isomers of 2-(1,2-dihydroxypropyl)- (**68a**) and 2-(2-hydroxy-1-methoxypropyl)-phenols (**68b**) (Scheme 44).

Scheme 44



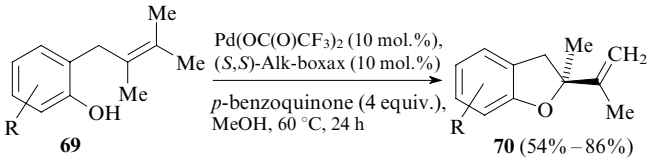
R = H (**a**, 35%), Me (**b**, 47%)

The authors believe that the formation of the products is preceded by isomerization of the allyl group to the propenyl

group and epoxidation. Indeed, the same products in the same ratio are obtained from 2-propenylphenol (**25a**).

An unusual method for the synthesis of heterocyclic oxygen- and nitrogen-containing compounds is intramolecular Wacker cyclization of unsaturated alcohols and amino alcohols of appropriate structure in the presence of palladium catalysts.[104] This reaction was used to prepare new dihydrobenzofuran derivatives from alkenylphenols. Cyclization of compounds **69** in the presence of palladium trifluoroacetate, (*S,S*)-2,2′-bis[(4-alkyl-4,5-dihydrooxazol-2-yl)]-1,1′-binaphthyl [(*S,S*)-Alk-boxax] as a chiral ligand and *p*-benzoquinone in methanol yielded compound **70** with high enantiomeric excess (94%–99% *ee*) (Scheme 45, the substituent positions in the starting phenol are indicated).

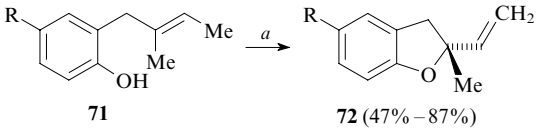
Scheme 45



R = H, 4-Me, 5-Me, 4-OMe, 5-OMe, 4-F, 4-Ph

Palladium(II)-catalyzed cyclization of substituted allylphenols **71** in a non-polar solvent (toluene) has been reported [104] (Scheme 46). In this case, the enantioselectivity was substantially lower: *ee* of product **72** was in the range from 20% to 90%.

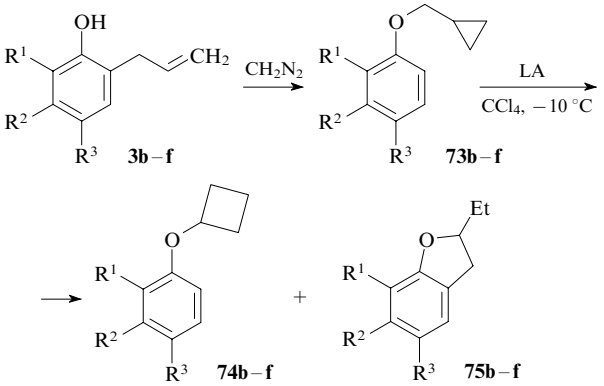
Scheme 46



R = H, Me, OMe, Bu^t, Ac;
(*a*) O_2 (1 atm.), $Pd(OC(O)CF_3)_2$ (10 mol.%), (−)-sparteine (100 mol.%), $Ca(OH)_2$ (2 equiv.), PhMe, 80 °C, 24–36 h

The reactions of *ortho*-, *meta*- and *para*-substituted allylcresols **3b–d** with diazomethane in the presence of palladium acetate afford cyclopropylmethyl phenyl ethers **73b–d** in moderate yields (Scheme 47).[105] The yield of ethers **73** increases to 81%–88% if brominated allylcresols **3e**,**f** are used. Further transformations of compounds **73** in the presence of Lewis acids (LA), BF_3 Et_2O, $AlCl_3$, $SnCl_4$, were studied. Under these conditions, isomerization of the cyclopropylmethyl moiety to give cyclobutyl phenyl ethers **74b–f** is accompanied by cyclization to 2-ethyl-2,3-dihydrobenzofurans **75b–f**.

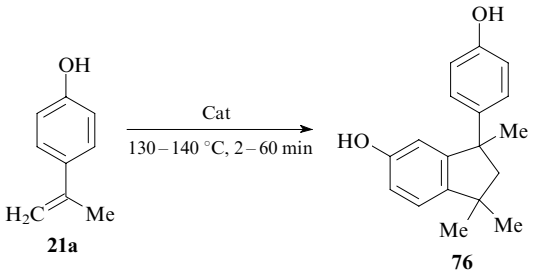
Scheme 47



$R^1 = R^2 = H$, R^3 = Me (**b**); R^1 = Me, $R^2 = R^3 = H$ (**c**);
$R^1 = R^3 = H$, R^2 = Me (**d**); R^1 = Br, $R^2 = R^3 = H$ (**e**);
$R^1 = R^2 = H$, R^3 = Br (**f**)

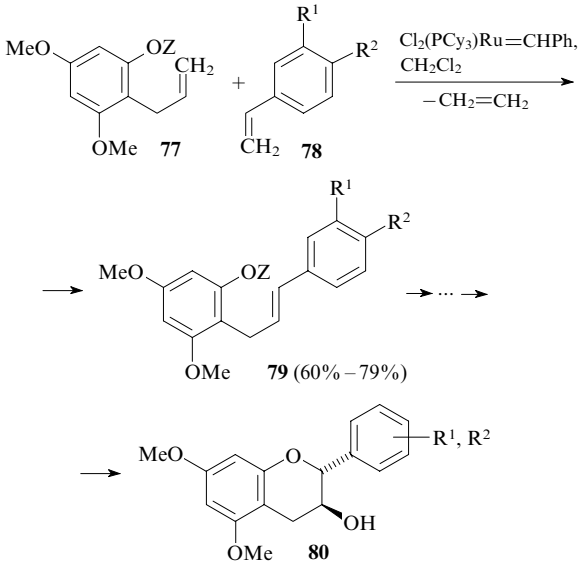
A patent [106] claims a method for preparing 3-(4-hydroxyphenyl)-1,1,3-trimethylindan-5-ol (**76**) by intramolecular cyclization of two 4-isopropenylphenol (**21a**) molecules in the presence of an acid catalyst (Cat = $AlCl_3$, Al_2O_3, SiO_2, *etc.*) at a temperature of 130–140 °C. It is noteworthy that this reaction catalyzed by boron trifluoride etherate gives product **76** in a high yield (89%) (Scheme 48).

Scheme 48



Forget-Champagne *et al.*[107] carried out selective cross-metathesis of protected 2-allylphenols **77** with styrene and its derivatives **78** in the presence of the Grubbs catalyst $Cl_2(PCy_3)Ru{=}CHPh$ (Cy is cyclohexyl) and obtained (*E*)-diarylpropene **79** (Scheme 49). These products can serve as the starting compounds for the synthesis of flavan-3-ols **80**.

Scheme 49

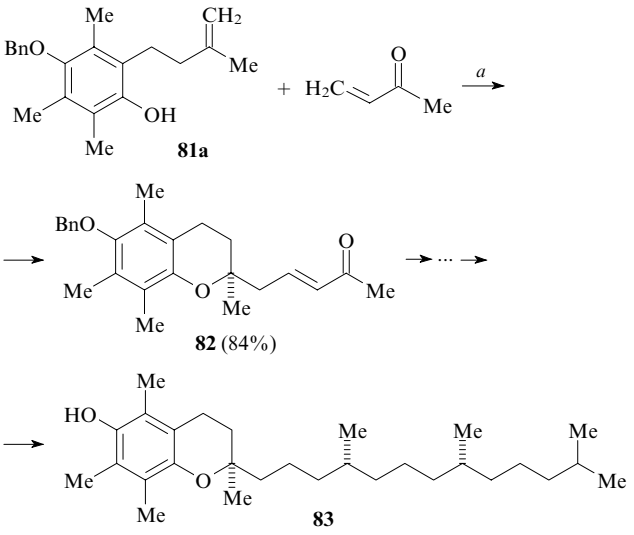


Z = Ac, methoxymethyl (MOM), triisopropylsilyl (TPS);
R^1 = H, NO_2; R^2 = H, Cl, OMe, CF_3; $R^1–R^2$ is benzo

An unusual domino reaction was accomplished by Tietze *et al.*[108–110] For the preparation of vitamin E and stereoselective synthesis of 4-dehydroxydiversonol, they studied the reaction of alkenylphenol **81a** with methyl vinyl ketone in the presence of a Pd^{II} catalyst. When palladium trifluoroacetate with a chiral ligand and *p*-benzoquinone were used, chromane **82** was prepared at room

temperature, and then it was converted to α-tocopherol (**83**) (Scheme 50).

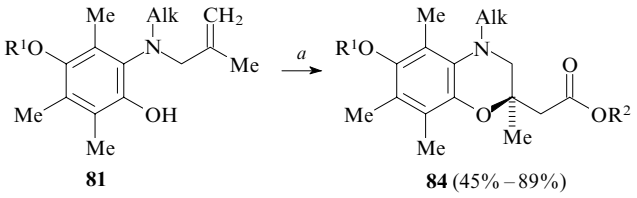
Scheme 50



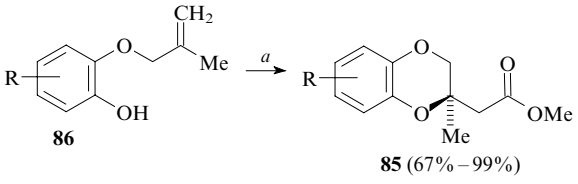
(*a*) $Pd(OC(O)CF_3)_2$ (10 mol.%), (*S*,*S*)-Bn-boxax (40 mol.%), *p*-benzoquinone (4 equiv.), CH_2Cl_2, rt

The sequence comprising the Wacker process and the Heck reaction yielded 2,3-dihydrobenz[1,4]oxazines (**84**) and 2,3-dihydrobenzo[1,4]dioxines (**85**) (Scheme 51).[111,112] Alkenylphenols **81** and ethers **86** with substituents in the aromatic ring were used as the starting compounds.

Scheme 51



R^1, R^2 = Me, Et;
(*a*) CO (1 atm.), $Pd(OC(O)CF_3)_2$ (10 mol.%), (*S*,*S*)-Bn-boxax (40 mol.%), *p*-benzoquinone (4 equiv.), R^2OH, rt or 60 °C

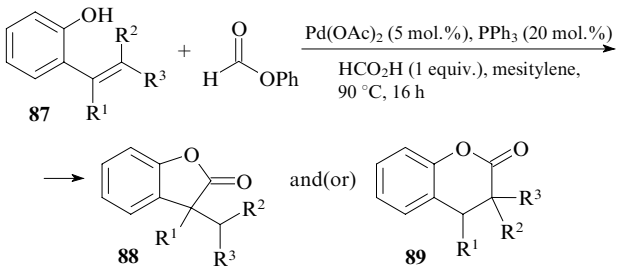


R = H, 2-OMe, 3-OMe, 5-Me, 4-Bu^t, 5-Bu^t;
(*a*) CO (1 atm.), $Pd(OC(O)CF_3)_2$ (10 mol.%), (*S*,*S*)-Bn-boxax (40 mol.%), *p*-benzoquinone (4 equiv.), MeOH, rt

Wang *et al.*[113] employed alkenylphenols **87**, phenyl formate and the $Pd(OAc)_2$–PPh_3 catalytic system to prepare benzofuran-2(3*H*)-ones **88** and 3,4-dihydrocoumarins **89** (Scheme 52). Depending on the starting phenol, either one of these lactones or a mixture of lactones was formed. Note that in the last 10–15 years, coumarins and their derivatives have been considered as intermediates in the synthesis of antimicrobial, antitumour and antiviral agents.[114]

Cyclocarbonylation reactions of 2-allylphenols in the presence of Pd/C and 1,4-bis(diphenylphosphino)butane as a ligand giving five-, six- and seven-membered lactones have been studied.[115]

Scheme 52

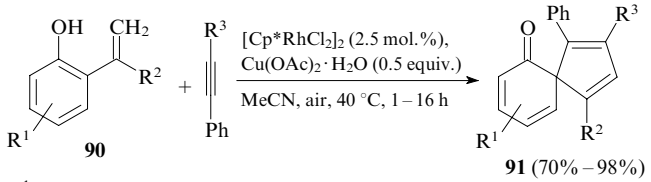


R^1 = H, Me, Ph; R^2 = H, Me, Pr^n, Pr^i; R^3 = H, Me, Ph, CO_2Et, *etc.*

Monti *et al.*[116] carried out photocyclization of 2-allylphenol and 2-allylaniline incorporated in cyclodextrin cavities. Study of the physicochemical properties of the products (2-methyl-2,3-dihydrofuran and -indole) demonstrated the formation of 1 : 1 complexes with the dextrin.

Reactions of 2-vinylphenols **90** with phenylacetylenes in the presence of ruthenium catalysts were investigated.[117] It was found that [3C + 2C]-annulation takes place under the reaction conditions due to oxidation and the reaction affords spirocyclic compounds **91** containing a quinoid moiety (Scheme 53).

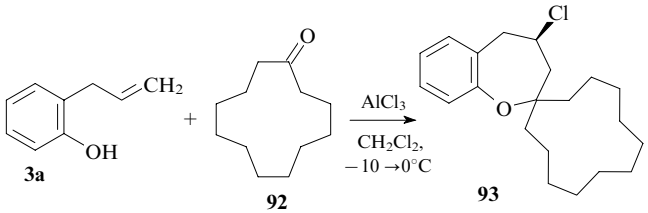
Scheme 53



R^1 = 4-Me, 4-OMe, 4-Br, 3-F, 3-Cl;
R^2 = Et, Ph, 4-$MeOC_6H_4$, 4-$CF_3C_6H_4$; R^3 = Et, Ph; Cp* = η^5-C_5Me_5

Prins cyclization of 2-allylphenol (**3a**) with macrocyclic ketone **92** in the presence of $AlCl_3$ has been reported.[118] The reaction is carried out under mild conditions and affords spirocyclic oxepine **93** with high stereoselectivity (Scheme 54). This process is distinguished by simplicity and high performance.

Scheme 54

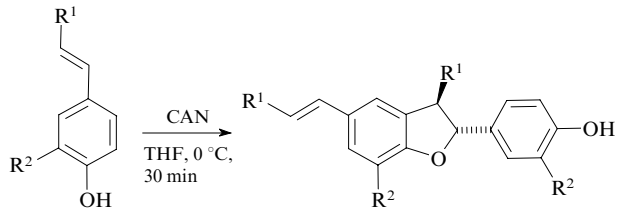


The Pauson–Khand reaction is suitable for the synthesis of tricyclic cyclopentenones, analogous to natural chromanes, from aromatic enynes.[119] A method based on this reaction for the synthesis of tricyclic compounds from alkenylphenols with the hydroxy group protected by a propargyl moiety has been developed.

Recently, the synthesis of *trans*-dihydrobenzofurans **94** by oxidative dimerization of *p*-alkenylphenols **95** in the

presence of cerium ammonium nitrate (CAN) has been reported [120] (Scheme 55). This method was used to prepare natural dihydrobenzofurans — (+)-conocarpan (R^1 = Me, R^2 = H) and (+)-licarin A (R^1 = Me, R^2 = OMe), while the subsequent methylation of the phenolic hydroxyl in licarin A gave (+)-acuminatin.

Scheme 55



95 **94** (81%–89%)

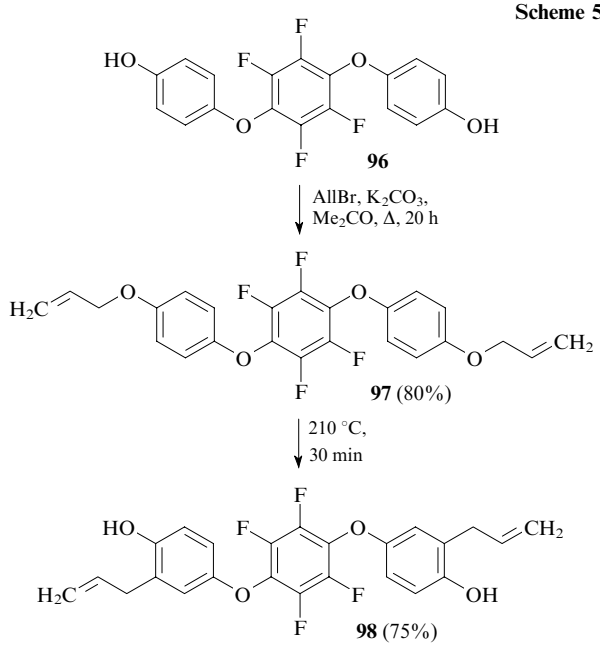
R^2 = H: R^1 = H, Me, Pr^i, Ac; R^2 = OMe: R^1 = H, Me, Ac

The presumed mechanism of the reaction is depicted in Scheme 56. Initially, under the action of CAN, the electron pair of the oxygen atom of phenol **95** forms a radical cation intermediate **A**, which is stabilized as resonance form **B**. The latter is cross-coupled with the starting phenol to yield intermediate **C**. This is followed by expulsion of a hydrogen atom to restore the aromaticity of the benzene ring in intermediate cation **D**. Intramolecular cyclization gives protonated dihydrobenzofuran **E** with *trans*-configured substituents, which is deprotonated giving rise to 2-substituted dihydrobenzofuran **94**.

VI. Syntheses based on diallylbisphenols

Allyl-containing bisphenols are valuable staring compounds for the preparation of thermally stable cross-linked polymer materials.[121, 122] In recent years, increasing attention has been devoted to the synthesis of allyl-containing bisphenols and polyaryl ethers based on them. Tkachenko *et al.*[122] described the allylation of fluorinated bisphenol **96**, resulting in diallyl ether **97**. Heating of **97** without a solvent induces migration of the allyl groups (Claisen rearrangement) to give fluorinated bisphenol with allyl groups — compound **98** (Scheme 57).

Scheme 57

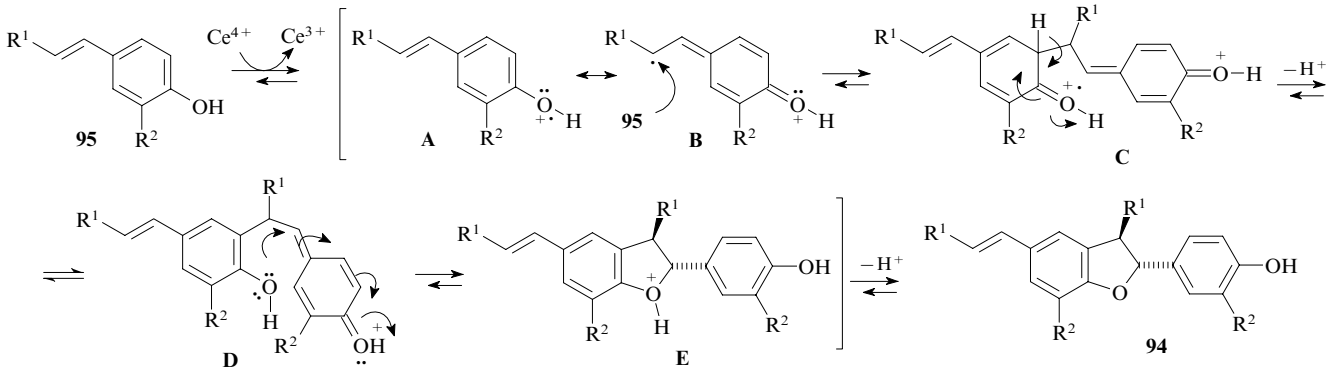


96 **97** (80%) **98** (75%)

The subsequent condensation of product **98** with decafluorobiphenyl (**99**) furnishes polyethers **100**, which are cured on heating (Scheme 58).[122] Polymer curing involves the allyl groups and affords a thermally stable material.[123] It is distinguished by relatively low dielectric permittivity;[124, 125] therefore, it can be used as a component of multilayer integrated systems.[126]

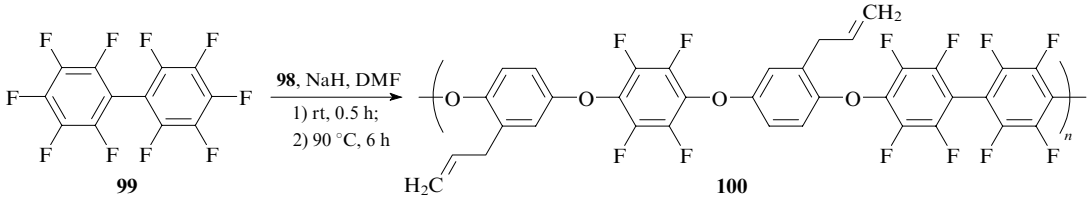
In the development of promising high-temperature matrices for carbon reinforced plastics meant for the modern aviation and aeronautics, a special role is allocated to the copolymers of diallyl-containing phenols with bis-maleimides. The cross-linked bis-maleimide polymers used

Scheme 56



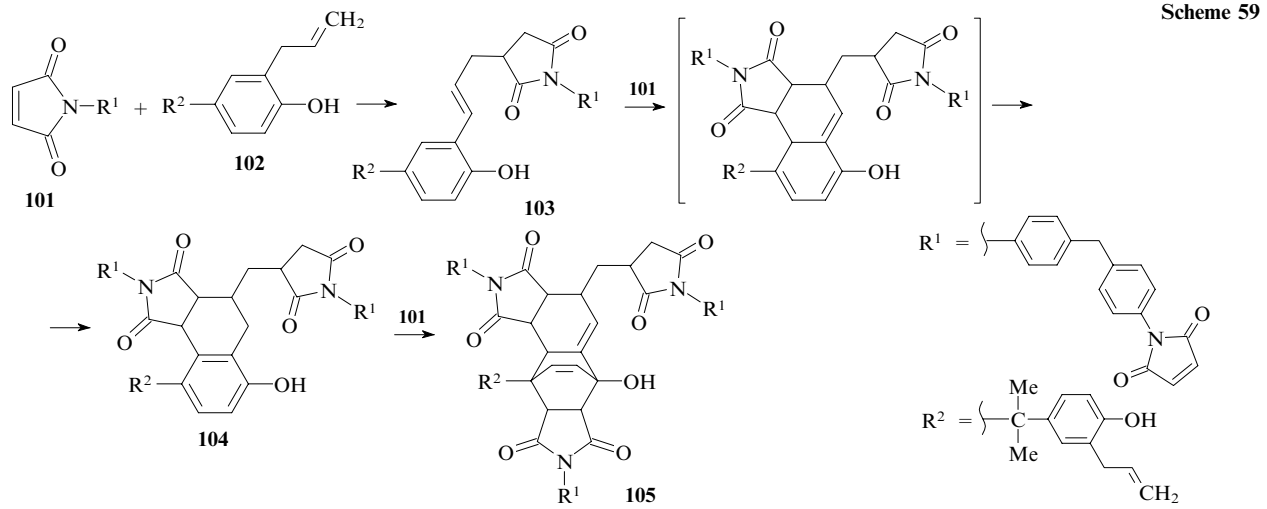
95 **A** **B** **C** **D** **E** **94**

Scheme 58



99 **100**

Scheme 59



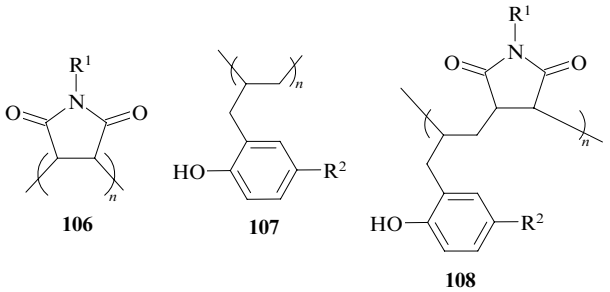
previously had a considerable drawbacks related to their brittleness and processing complexity.[127–130] Combination of maleimides with diallyl-bisphenols may provide the formation of high-temperature materials possessing a set of valuable properties.

The reactions of 4,4′-bis(maleimido)diphenylmethane (**101**) with various diallyl-bisphenols have been studied.[131–133] For model compounds, for example, bisphenol **102**, thermal curing of coupling product **103** was investigated by isothermal calorimetry. Curing occurs in two temperature ranges, the highest rate being observed in the 230–240 and 330–340 °C ranges corresponding to the two principal reactions: condensation of the maleimide and allyl groups and subsequent cross-linking. The latter reaction occurs as radical polymerization involving the propenyl groups formed in the first step and unreacted allyl groups.

Presumably,[131] curing of the system starts with the addition of the allyl group of phenol **102** to the maleimide moiety of imide **101** to give the 1 : 1 alkene adduct (**103**) (Scheme 59). Then adduct **103** undergoes the Diels–Alder reaction with a second molecule of maleimide **101**, resulting in the formation of 2 : 1 adduct **104**. In the authors' opinion, the formation of a 3 : 1 adduct (**105**) is also possible (see Scheme 59).

Apart from the polycondensation type reactions presented above, thermal initiation can also induce homopolymerization of the initial monomers, which gives polymers **106** and **107**. Owing to electron-withdrawing properties of the maleimide group, maleimide **101** can copolymerize with various unsaturated compounds, for example bisphenol **102**, to give copolymer **108**.

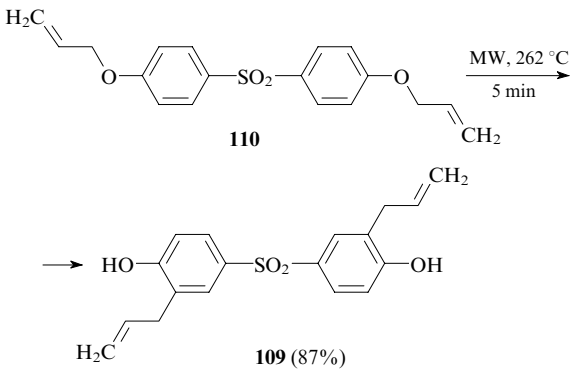
Structures 106–108



The enthalpy of condensation and polymerization involving the double bond of the maleimide moiety and the allyl group was calculated[132] to be 92 kJ mol^{-1}. The experimental results also indicate that first, condensation of the allyl and maleimide groups occurs to give linear polymers and then they are cross-linked. The latter process involves the propenyl groups that formed in the first reaction. Partial homopolymerization of maleimide also takes place.[133]

Yamamoto *et al.*[134] synthesized bis(3-allyl-4-hydroxyphenyl) sulfone (**109**) by the Claisen rearrangement of bis(4-allyloxyphenyl) sulfone (**110**) under microwave radiation (MW) without a solvent for 5 min (Scheme 60).

Scheme 60



In the authors' opinion, the reaction is stepwise: one allyl group migrates first, and then the other group migrates. The yield of product **109** is fairly high. It is noteworthy that with convective heating, this reaction requires a rather long time (from 2 to 30 h).

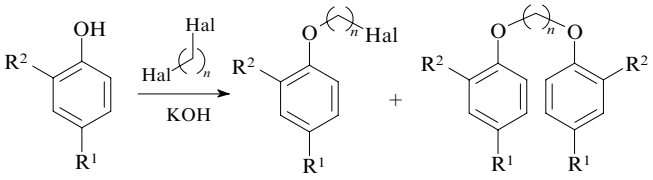
VII. Reactions of alkenylphenols with dihaloalkanes

Among the interesting transformations of alkenylphenols, mention should be made of their reactions with symmetric dihaloalkanes (Williamson reaction), resulting in the formation of bifunctional compounds. These compounds are suitable as cross-linking agents in the synthesis of structured polymeric materials based on vinyl monomers. It is worth noting that depending on the purpose of the material,

hyper-cross-linked polymers are needed in some cases and low cross-linking degrees are required in other cases.[135]

Bayramov and co-workers[136, 137] studied the condensations of compounds **3a**, **21a** and **25a** with dihaloalkanes promoted by KI in the presence of aqueous KOH (Scheme 61). This reaction was found to yield two types of compounds — (alkenylphenoxy)haloalkanes **111a–c** and bis(alkenylphenoxy)alkanes **112a–c**, their yields being mainly dependent on the molar ratio of reactants and remaining virtually unchanged upon variation of the halogen atom. As an example, Table 1 presents the results of reactions of alkenylphenols with 1,4-dibromobutane.

Scheme 61



3a, **21a**, **25a** **111a–c** **112a–c**

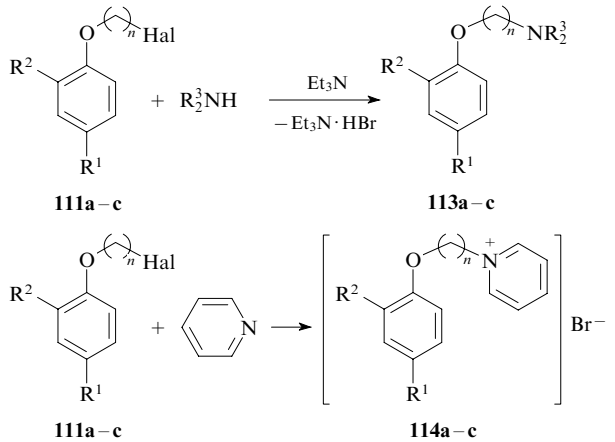
111, **112**: R^1 = H: R^2 = $CH_2CH{=}CH_2$ (**a**), CH=CHMe-(*E*) (**b**); R^1 = C(Me)=CH_2, R^2 = H (**c**); *n* = 2–4, 10

Table 1. Optimal conditions of reactions of compounds **3a**, **21a** and **25a** with 1,4-dibromobutane [KOH (aq.), KI, 80 °C, 0.5 h].

Alkenylphenol	Dibromide : phenol ratio (mol.)	Products **111**, **112**	Yield (%)	
			111	**112**
3a	1 : 3	**a**	0	78.0
	2 : 1	**a**	57.0	0
21a	1 : 3	**b**	0	90.6
	3 : 2	**b**	64.2	18.1
25a	1 : 3	**c**	2.7	88.0
	2 : 1	**c**	67.9	1.6

Compounds **111** containing an active halogen atom easily react with amines (in the presence of triethylamine) and pyridine to give amino derivatives **113** and pyridinium salts **114** (Scheme 62).

Scheme 62



111a–c **113a–c**

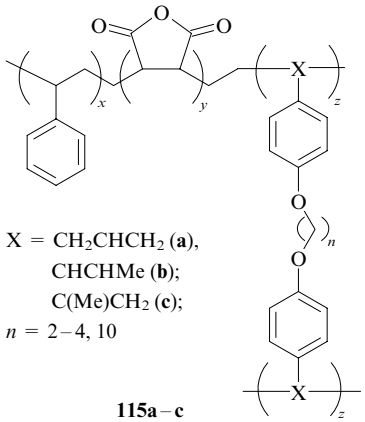
111a–c **114a–c**

R^1 = H: R^2 = $CH_2CH{=}CH_2$ (**a**), CH=CHMe-(*E*) (**b**); R^1 = C(Me)=CH_2, R^2 = H (**c**); *n* = 2–4, 10; R^3 = Et; R^3–R^3 = $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$

Products **113** and **114** were found to be effective corrosion inhibitors for metals in aqueous saline and acidic media.[138, 139]

Dimers **112a** were utilized as cross-linking comonomers in the synthesis of three-dimensional copolymers. By radical copolymerization of styrene with maleic anhydride in the presence of 1,4-bis(alkenylphenoxy)butane, structured copolymers **115a–c** were obtained.[140]

Structures 115



X = CH_2CHCH_2 (**a**), CHCHMe (**b**); C(Me)CH_2 (**c**); *n* = 2–4, 10

115a–c

After hydrolysis, these cross-linked copolymers show complexing properties towards uranyl ions and can find use as sorbents for cleaning water systems from uranium compounds.[141]

Compounds **112a** (R^1 = H, R^2 = All: *n* = 4, 10) were studied by X-ray diffraction after thorough purification by recrystallization from octane and nonane (Figs 1, 2). The crystals of **112a** (*n* = 4) are orthorhombic, while the *n* = 10 homologue crystallizes in the monoclinic system.[142, 143]

Crivello *et al.*[144, 145] synthesized bifunctional dimers **112** in a different way, namely, by condensation of dibromoalkanes with isoeugenol (**116**) and allylphenol **3a** under the action of aqueous NaOH in the presence of a quaternary ammonium salt as the catalyst (Scheme 63). However, the yields of the final products were moderate under these conditions.

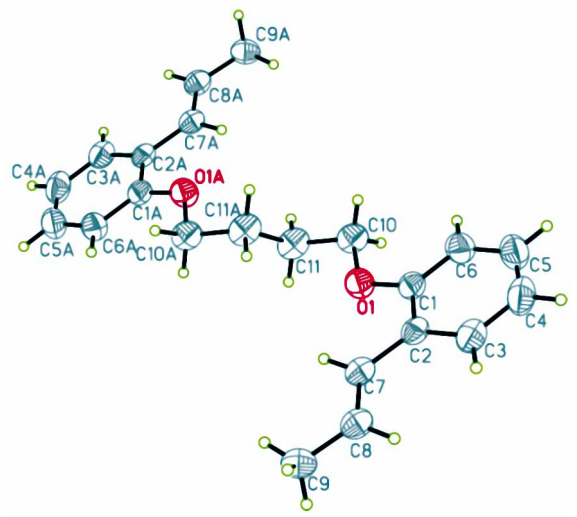


Figure 1. Molecular structure of **112a** (*n* = 4) in the crystal.[142]

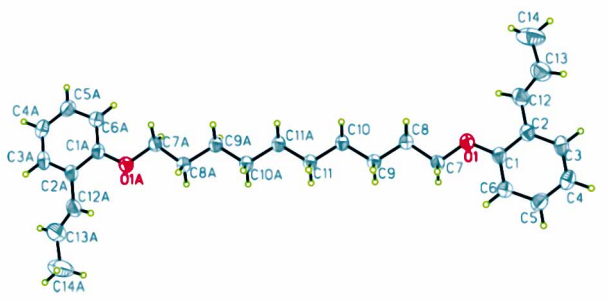
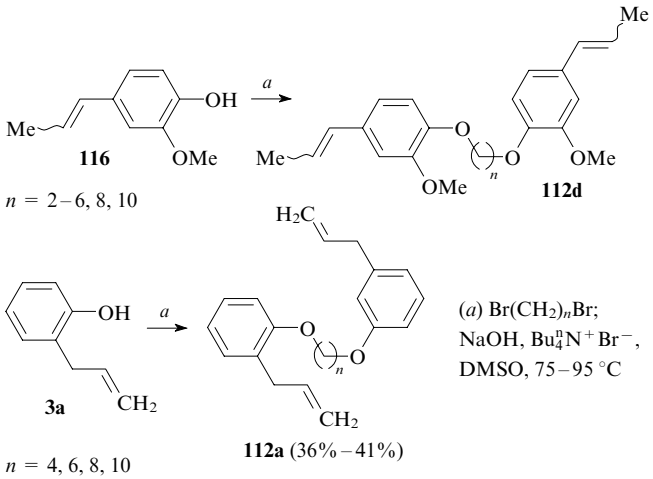


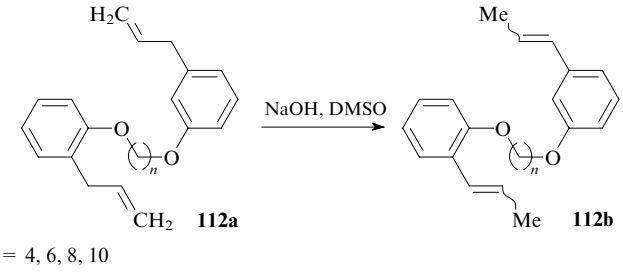
Figure 2. Molecular structure of **112a** (n = 10) in the crystal.[143]

Scheme 63



In addition, condensation may be accompanied by isomerization of the allyl group to a propenyl group, as was actually observed by the authors (Scheme 64).

Scheme 64



Bifunctional monomers **117** and **118** similar to compounds **111** were obtained by the condensation of alkenylphenols **116** and **3a** with vinyl 2-chloroethyl ether (Scheme 65).[145] In the presence of a Ru^{II} catalyst, compound **118** isomerizes to **119**.

These monomers are formed in good yields and are low-melting compounds. Photopolymerization of the bifunctional monomers synthesized by condensation of alkenylphenols and eugenol with α,ω-dibromoalkanes in the presence of a photoinitiator, for example, (4-n-octyloxyphenyl)phenyliodonium hexafluoroantimonate (0.5 mol.%) resulted in the formation of materials having good thermal properties.

VIII. Applications of modified polymers and copolymers based on alkenylphenols

The modified copolymers of vinyl- and isopropenylphenols with various comonomers are widely used as composite materials meant for the manufacture of integrated circuits in microelectronics, UV light reflectors, negative photoresists and so on.[146–149] Bipolymers are often obtained using methacrylates[150–153] and their methyl and n-butyl derivatives as comonomers, while terpolymers are prepared with styrene and substituted (meth)acrylates.[154–156] In some cases, isobornyl[157,158] or adamantly substituents[159] are introduced into the comonomer molecules.

The Maruzen Petrochemical company developed[160] a method for the preparation of a high-molecular-mass compound distinguished by an enhanced transmission coefficient for the visible and far-UV light. This polymer is formed upon radical or cationic polymerization of 4-vinylphenol or copolymerization of 4-vinylphenol with other monomers produced on a large scale: styrene or acrylic/methacrylic acid.

The Tokyo Ohka Kogyo company proposed a composition for semiconductor devices and liquid-crystal displays consisting of polyvinylphenol, styrene–acrylic acid copolymer, novolac resin and compounds with quinone diazide groups.[161]

Bipolymers (**120**) and terpolymers (**121**) of alkenylphenols containing diazonaphthoquinonesulfonyl substituents in combination with polymers **122**, which were prepared by polycondensation of phenols and their diazonaphthaquinonesulfonyl-substituted derivatives with formaldehyde, were proposed as materials for the manufacture of antireflective coatings for semiconductor devices.[162]

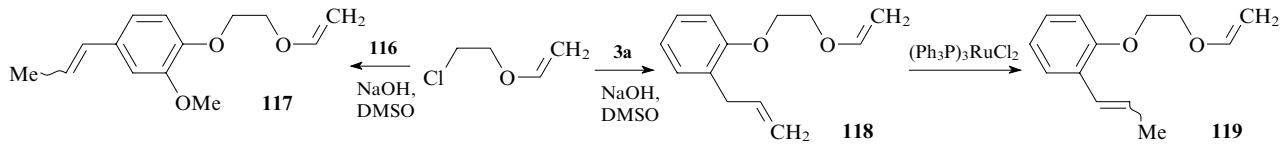
Copolymers of vinyl- or isopropenylphenols with (meth)acrylates having molecular masses from 1 to 500 kDa partly cross-linked *via* hydroxy groups also possess properties of photoresists.[163]

A radiation-sensitive polymer composition possessing high insulating properties was prepared by the coupling of polyvinylphenol with various rubbers chemically modified with epoxide compounds. This composition also includes a cross-linking component (amino resin) and photopolymerization initiators — metallocenes, sulfonium or diazonium salts.[164]

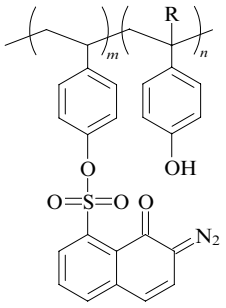
Researchers of NEC Electronics and Vamana Metsuharu[165] developed a new polymer composition containing 10%–20% of 4-vinylphenol copolymer **123** to produce a material with photoresist properties.

The molecular mass of this copolymer is 5 to 20 kDa. The composition also contains 1%–15% of a photogenerator of acid (sulfonium or iodonium compound) and 0.5%–6% of polystyrene as a filler.

Scheme 65

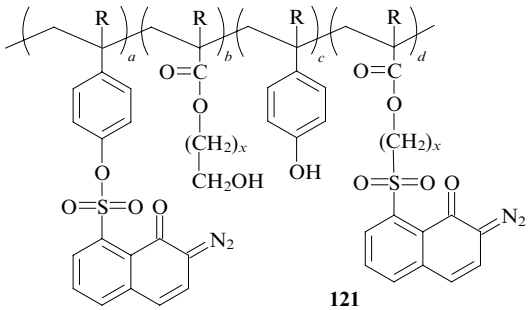


Structures 120 – 124



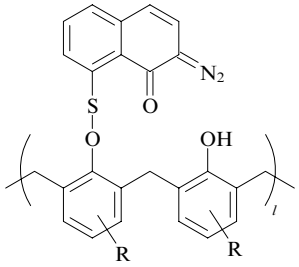
120

R = Alk (C_1–C_6), OH, CH_2OH;
$m:n$ = (0.1–0.9):(0.1–0.9)

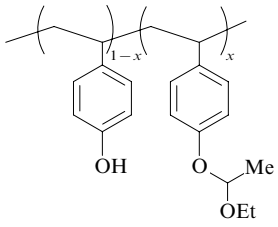


121

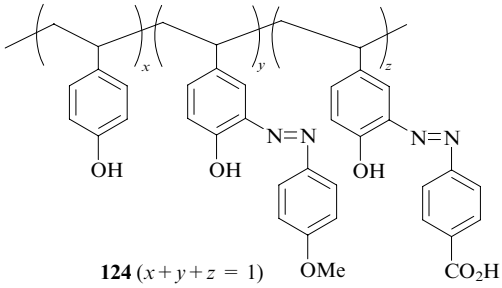
R = Alk (C_1–C_6), OH, CH_2OH;
$a:b:c:d$ = (0.1–0.9):(0.1–0.9):(0.1–0.9):(0.1–0.9); x = 1–5



122 (R = Me, OH; $l > 1$)



123



124 ($x+y+z$ = 1)

Polymers **124** containing azo dye moieties often used in ptotoresist compositions were obtained by reactions of polyvinylphenols with diazonium salts.[166]

Polyvinylphenols in which hydroxy groups are partially or fully protected proved to be useful in the manufacture of integrated circuits for microelectronics. *tert*-Butoxycarbonyl, trialkyl(aryl)silyl or acetyl groups capable of decomposing under the action of acid generated by onium salts on exposure to actinic radiation were employed as protective groups.[167]

Cao *et al.*[168] proposed a new method for the synthesis of poly(4-vinylphenol). The authors carried out first radical polymerization of 4-methoxystyrene and then dealkylation giving rise to the target polymer. Numerous ultrathin films were produced from a mixture of poly(4-vinylphenol) and diazo resins. To prepare the films, the composition was cured by exposure to UV radiation. Under these conditions, chemical reaction took place involving the diazonium group of the diazo resin and the hydroxy group of poly(4-vinylphenol).

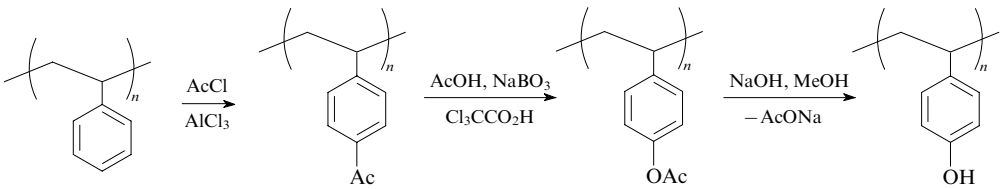
One more method for the preparation of poly(4-vinylphenol) was reported by Deokar *et al.*[169] Polystyrene with molecular mass of 3 to 50 kDa served as the starting compound. It was introduced into the following sequence of reactions: acetylation with acetyl chloride in carbon disulfide or in cyclohexane, oxidation with sodium perborate in the presence of trichloroacetic acid and, finally, hydrolysis of acetoxy groups with a methanol solution of NaOH (Scheme 66). The authors developed a photoresist material for the use in photolithography based on the prepared poly(4-vinylphenol).

Polyvinylphenols and their graphitized forms are organic dielectrics; they found use in electronics for the manufacture of transistors.[170, 171]

A promising application of polyvinylphenols is for the production of polymer type sensors. The composite films obtained from single-walled carbon nanotubes coated by molecularly imprinted poly(4-vinylphenol) were studied by UV and IR spectroscopy.[172] The spectra confirmed the successful molecular imprinting of this film with the alkaloid cotinine. The electrical resistance of the imprinted film was shown to substantially change upon binding of cotinine (by >30 kΩ); upon removal of the alkaloid, the resistance of the film returns to the initial value.

It is noteworthy that the chemical amplification concept proposed by researchers of IBM (International Business Machines, USA) played an important role in the design of photoresist materials possessing high resolution capability, plasmochemical stability and other valuable properties.[173] It was shown that, apart from the polymer component with specified properties, the composition must contain a photochemically generated acid (usually, diaryliodonium or triarylsulfonium derivatives). The chemical amplification mechanism was studied for the first time in relation to the reaction of poly(*tert*-butoxycarbonyloxystyrene) (**125**) in the presence of the

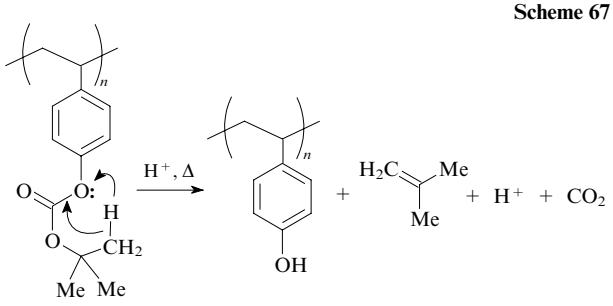
Scheme 66



sulfonium salt [4-$Ar_2S^+C_6H_4SC_6H_4S^+Ar_2$-4]$(SbF_6^-)_2$ — [4-$ArSC_6H_4S^+Ar_2$-4]$\cdot SbF_6^-$ = 90 : 10. Under photochemical conditions, this salt eliminates a proton, which promotes hydrolysis of polymer **125** to give poly(4-vinylphenol) (Scheme 67).

The acid-catalyzed hydrolysis of the polymer upon photolysis of the sulfonium salt was monitored by UV and IR spectroscopy. The acid formed takes part in the hydrolysis of the polymer only as a result of post-exposure heating.

Scheme 67



125

Currently, poly(4-vinylphenol) is also used as a model in the studies aimed at elucidation of the kinetic patterns of chemical amplification in various systems.

* * *

As can be seen from the above, the chemistry of alkenylphenols is permanently developing, which is caused by extensive opportunities for carrying out various transformations involving these compounds owing to the presence of several reaction centres in their molecules. Many of the nitrogen-, sulfur- and phosphorus-containing monomers obtained from these compounds can be used as stabilizing agents for polymeric materials, inhibitors of metal corrosion and lubricating oil additives.

It is difficult to overestimate the role of alkenylphenol-based polymers and copolymers with vinyl and other comonomers in the design of modern computers. Further research in this field of chemistry will undoubtedly enable the development of new composite materials for various purposes with practically valuable properties.

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