Chemistry of Heterocyclic Compounds, Vol. 32, No. 7, 1996

FURAN DERIVATIVES OF GROUP VI ELEMENTS (REVIEW)

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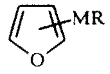
Methods of synthesis and the physical and chemical properties of the furan derivatives of selenium, tellurium, chromium, molybdenum, and tungsten are reviewed.

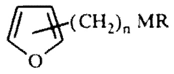
Earlier in a series of reviews [1-4] we discussed published data and the results of our own researches on the synthesis and properties of the furan derivatives of metals of groups I-IV of the periodic system, while in [5] we examined not only the organometallic compounds of the elements of group V but also the derivatives of phosphorus. The present review, devoted to the furan compounds of group VI, examines the derivatives of selenium, tellurium, chromium, molybdenum, and tungsten. The results of investigations into the organosulfur derivatives are not included on account of the enormous amount of material that has accumulated on this subject.

1. DERIVATIVES OF SELENIUM AND TELLURIUM

The furan derivatives of selenium and tellurium can be subdivided into three main types, i.e., compounds with a C_{furyl}—M bond (I) and derivatives in which the element is separated from the ring by a carbon chain (II) or by a carbofunctional group (III). There are few compounds of type (III) [6-8], and they are as a rule organophosphorus derivatives. Methods for their preparation and their physicochemical properties were examined in [5], and only compounds of types (I) and (II) are represented in the present review.



I



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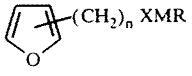
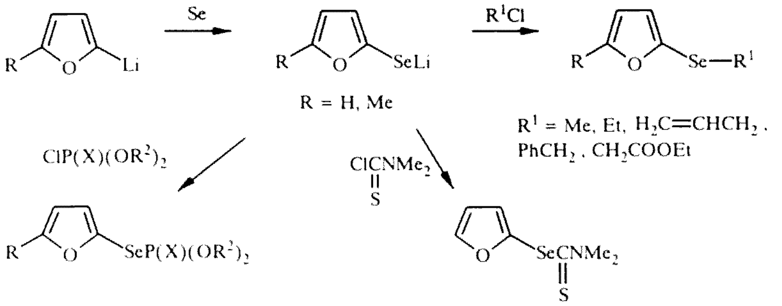


III

1.1. Synthesis of Compounds of Type (I)

The main method for the production of the furan derivatives of selenium [9-16] and tellurium [17] with a C_{furyl}—M bond is the lithium synthesis. The reaction of 2-furyl- and 5-methyl-2-furyllithium with elemental selenium leading to lithium furyl selenides, which in turn react readily with halogen-containing compounds, is usually employed. Not only alkyl [9, 14, 15], aryl [16], and carbofunctional [10, 14, 15] derivatives but also organoselenophosphorus derivatives of furan [11, 12] were obtained in this way.



Latvian Institute of Organic Synthesis, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 867-895, July, 1996. Original article submitted March 6, 1996.

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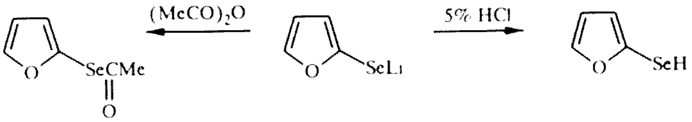
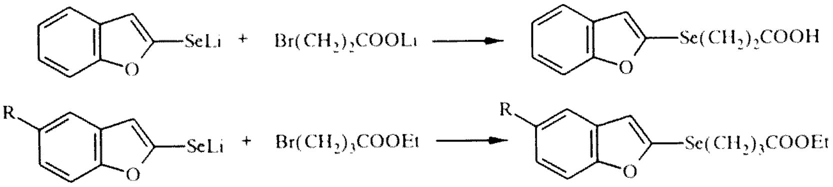
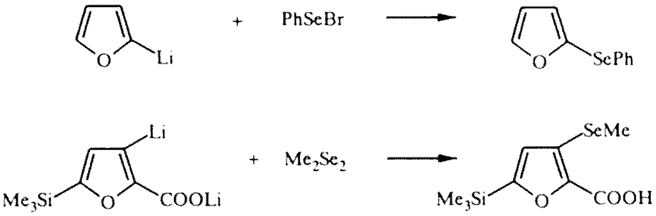
The hydrolysis of lithium furyl selenide with a 5% solution of hydrochloric acid gave furylselenol, and acylation with acetic anhydride gave a 64% yield of furyl acetyl selenide [15].



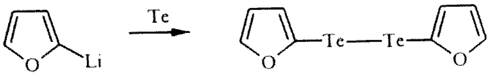
Lithium benzofuryl selenides are alkylated with 60-70% yields by lithium 3-bromopropionate and 4-bromobutyric esters [18].



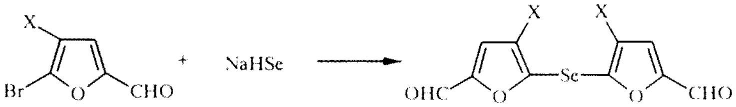
Furyl selenides can also be obtained in the reaction of the lithium derivatives of furan with phenylselenium bromide [16] and dimethyl diselenide [13].



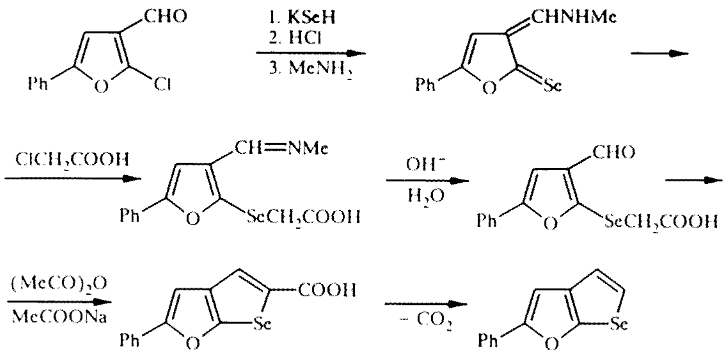
Difuryl ditelluride is formed with a 60% yield when 2-furyllithium is treated with tellurium in tetrahydrofuran with slight cooling [17].



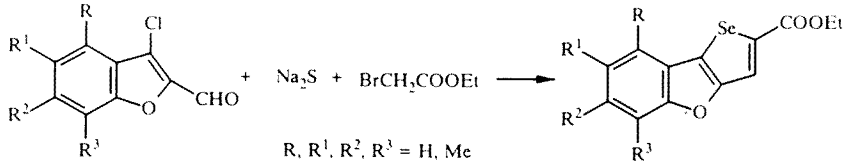
In addition to the lithium synthesis, the reaction of halogenofurans with sodium [19] and potassium [20] hydroselenides has also been used for the synthesis of furyl selenides. Thus, the action of sodium hydroselenide on 5-bromo- and 4,5-dibromofurfural in water leads to the initial formation of sodium 2-formyl-5-furyl selenides, which are strong nucleophiles and react instantaneously with the initial bromine-containing furfurals, giving 50-54% yields of difuryl selenides [19].



The reaction of chloroacetic acid with 4-aminomethylene derivatives of 5-selenofuranone, synthesized from 2-chloro-3-formyl-5-phenylfuran by the action of potassium hydroselenide, acid hydrolysis, and condensation of the carbonyl group with methylamine, takes place at the C=Se group [20, 21]. Subsequent cyclization of the product in acetic anhydride in the presence of sodium acetate gave 2-phenylselenopheno[2,3-*b*]furan-5-carboxylic acid and its decarboxylation product in a ratio of 2:1 [20, 21].

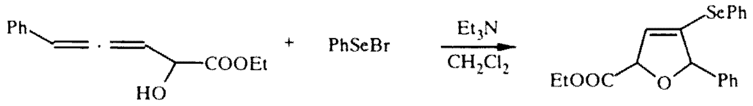


Compounds in which the benzofuran ring is condensed with the selenophene ring were synthesized in a similar way [22].

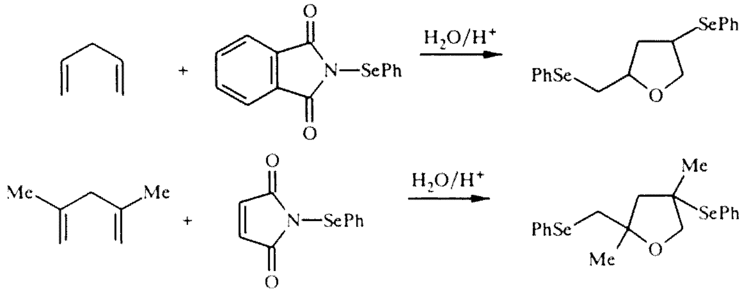


In most cases tetrahydrofuran and dihydrofuran derivatives with a $C_{heterocycle}$—Se bond were obtained by the cyclization of unsaturated compounds and oxiranes [23-29] with various selenium compounds.

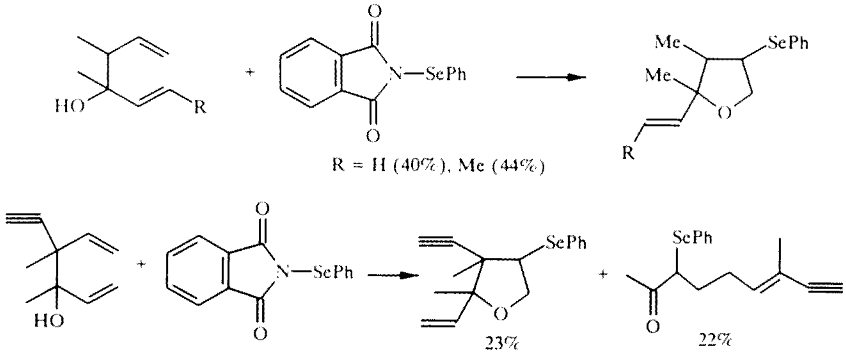
Allenes containing a hydroxymethyl substituent readily undergo cyclization to 2,5-(3-phenylseleno)dihydrofurans under the influence of phenylselenium bromide and triethylamine in methylene chloride at room temperature [23].



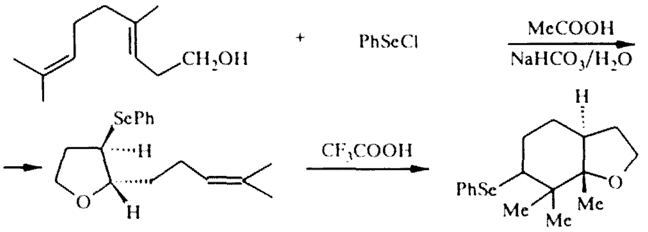
N-Phenylselenophthalimide and N-phenylselenosuccinimide react with olefins at 25°C in methylene chloride in the presence of 2 to 3 times the amount of water and an acid catalyst, such as p-toluenesulfonic acid. Various derivatives of tetrahydrofuran are obtained with yields of 24-55% [24].



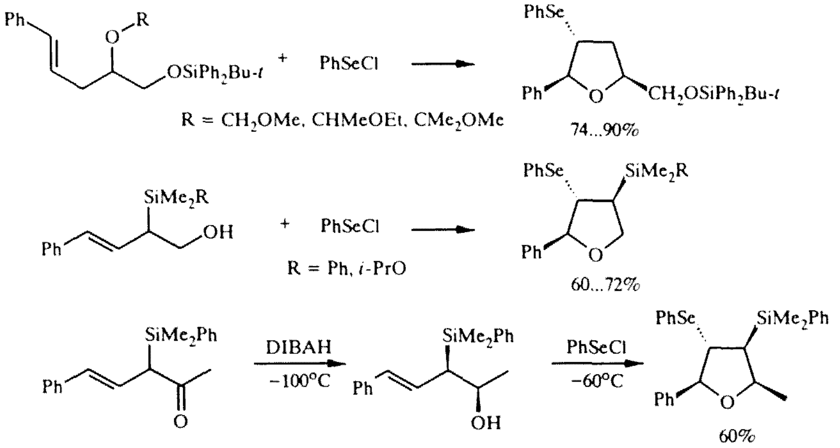
N-Phenylselenophthalimide is also a fairly effective O-cyclizing agent for 1,5-hexadien-3-ols. As in the previous case, the reaction takes place in the presence of p-toluenesulfonic acid [25].



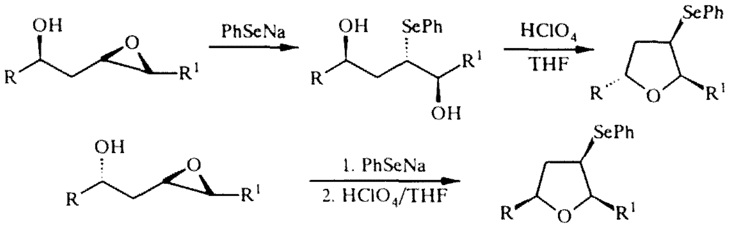
4,8-Dimethylnona-3,7-dien-1-ol undergoes cyclization in 6 h under the influence of phenylselenium chloride in acetic acid to 3-phenylseleno-substituted 2-(4-methyl-3-pentenyl)tetrahydrofuran, which gives a bicyclic product almost instantaneously with a yield of 70% when treated with trifluoroacetic acid [26].



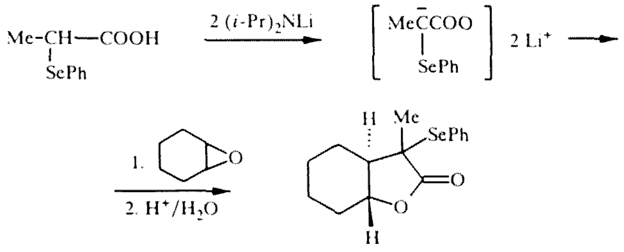
The cyclization of the *tert*-butyldiphenylsilyl ethers of 5-phenyl-2-alkoxymethoxy-4-penten-1-ols [27], 5-phenyl-2-RMe_2Si-4-penten-1-ols [28], and 1-phenyl-2-$PhMe_2Si$-1-penten-4-ol [28] with phenylselenium chloride takes place with high selectivity and yield. Tetrahydrofuran derivatives with three and four chiral centers in the ring were synthesized in this way.



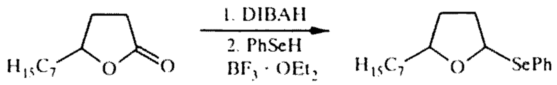
The action of sodium phenyl selenide on hydroxyethyloxiranes leads initially to opening of the oxirane ring and the formation of phenylselenodiols, in which the hydroxyl groups are separated by four carbon atoms. It was then possible as a result of the action of perchloric acid on the diols in tetrahydrofuran to close the chain into a five-membered tetrahydrofuran ring [29].



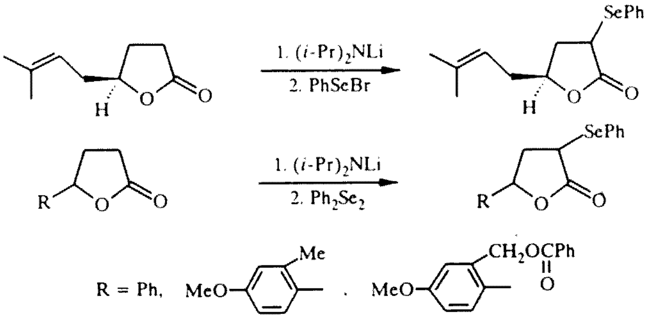
The dilithium derivative of α-phenylselenopropionic acid reacts stereoselectively with cyclohexene oxide; the phenylselenium derivative of a γ-lactone with a condensed cyclohexane ring is formed with a 54% yield [30].



It was possible to introduce a phenylselenium group into the tetrahydrofuran ring by reducing 4-heptyl-4-butanolide with diisobutylaluminum hydride to the corresponding alcohol and then substituting the hydroxyl group by the action of phenylselenone in the presence of boron trifluoride etherate. 2-Heptyl-5-phenylselenotetrahydrofuran was obtained in this way with an almost quantitative yield [31].

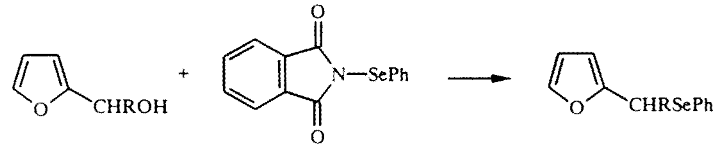


The anions of various 4-substituted 4-butanolides, which can be obtained as a result of the action of lithium diisopropylamide on butyrolactone, are easily selenated with phenylselenium bromide [32] and dimethyl selenide [33]. In this method the yield of 2-phenylseleno-4-butanolides exceeds 80%.



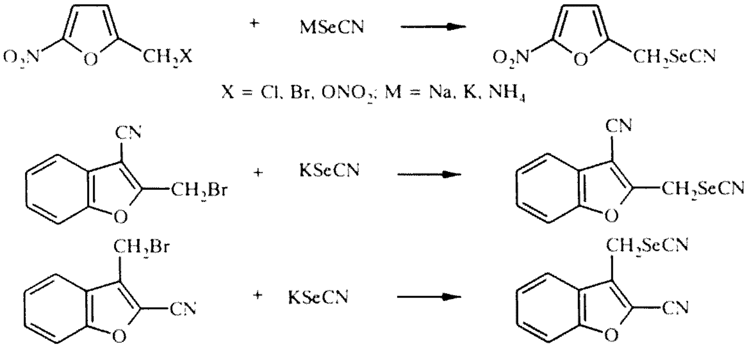
1.2. Synthesis of Compounds of Type (II)

A convenient method for the synthesis of furfuryl selenides is the selenation of furfuryl alcohol and its derivatives with N-phenylselenophthalimide. Phenyl furfuryl selenides were obtained by this method with yields of more than 70% [16].

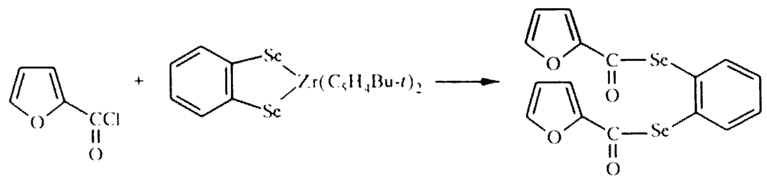


R = H, $PhCH_2CH_2$

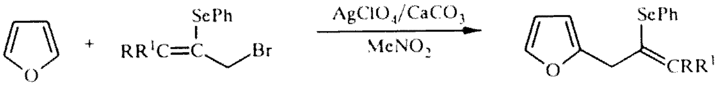
The halogen atom in halogenomethyl derivatives of 5-nitrofuran [34] and cyanobenzofurans [35] can be substituted by a cyano group by the action of the cyanoselenides of alkali metals. 5-Nitro-2-furfuryl nitrate enters into a similar reaction [34].



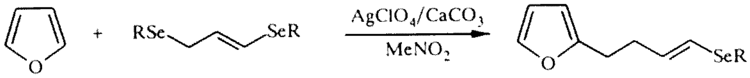
1,2-Di(2-furoyl)selenobenzene was synthesized with a 68% yield from a zirconium complex containing 1,2-diselenobenzene as ligand and 2-furoyl chloride in tetrahydrofuran at room temperature [36].



Allyl cations, stabilized by the seleno group, are easily formed by the action of silver perchlorate and a weak base (calcium carbonate) in nitromethane with cooling to −15°C on 3-bromo-2-phenylseleno-1-propenes [37] and 1,3-di(methylseleno)- and 1,3-di(phenylseleno)propenes [38]. The obtained cations react with furan, giving the products from electrophilic substitution.

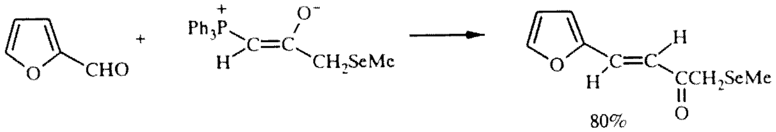


$R = R^1 = H$; $R = H, R^1 = Cl$; $R = H, R^1 = Br$;
$R = R^1 = Me$; $R = H, R^1 = Et$ (yield 58...65%)

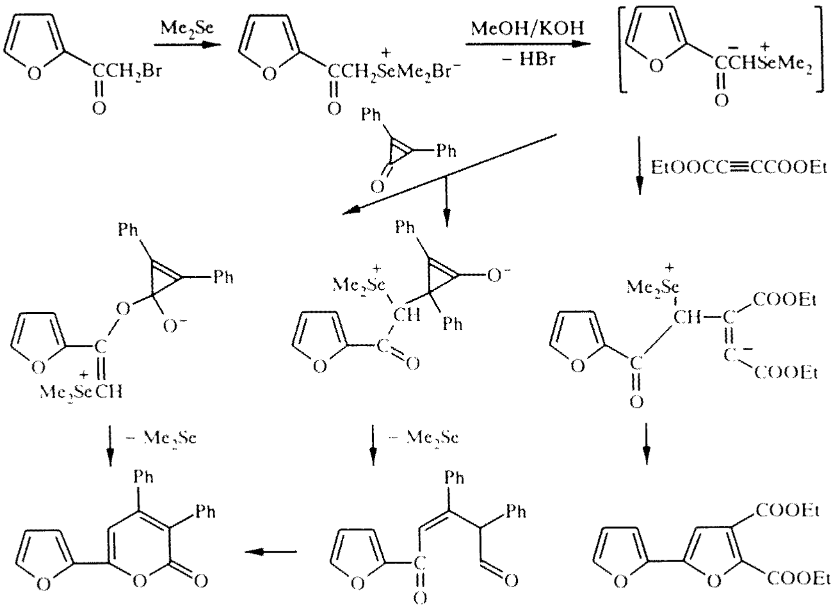


R = Me, Ph (yield 24...50%)

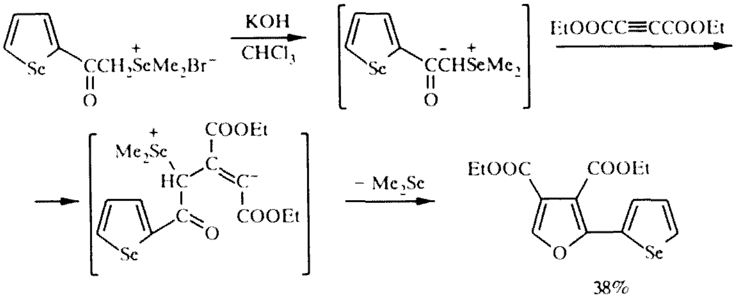
The Wittig reaction between furfural and methylselenoacetylmethylenetriphenylphosphorane at room temperature in the presence of a small amount of benzoic acid was used for the synthesis of 2-furylvinyl methylselenomethyl ketone. The obtained α,β-unsaturated ketone had the *trans* configuration [39].



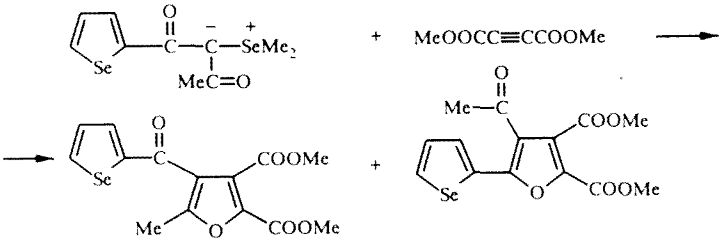
The reaction of bromomethyl 2-furyl ketone with an equivalent amount of dimethyl selenide in nitromethane gives a high yield of the selenonium salt dimethyl(2-furoylmethyl)selenonium bromide [40]. The imide of this compound has been used for the production of various heterocycles [40-43].



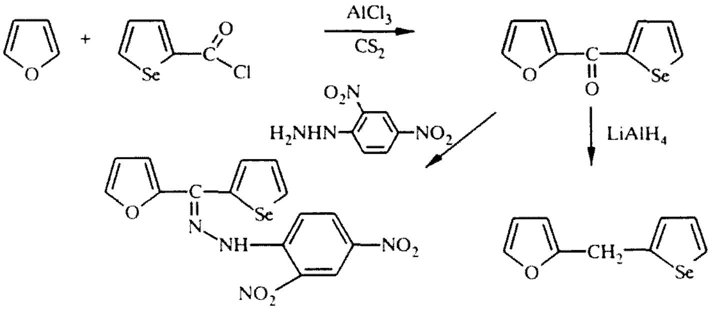
The analogous selenonium salt containing a selenophene fragment instead of the furyl group enters into cyclization with acetylenedicarboxylic esters [43] with the formation of furylselenophenes.



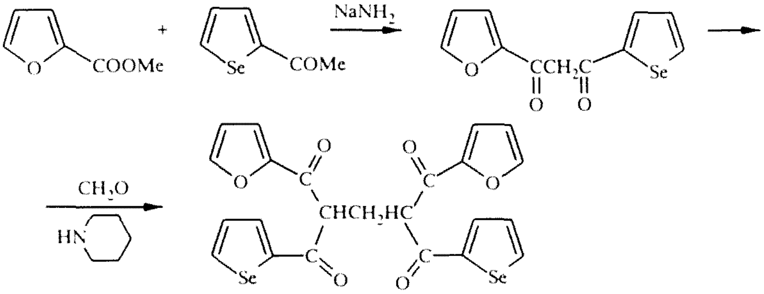
If an acetyl group is introduced into the methylene group of the selenonium salt, cyclization during the condensation with dimethyl acetylenedicarboxylate takes place at both carbonyl groups, and a mixture of furoylselenophene and furylselenophene in a ratio of 3:2 is formed with an overall yield of 89% [44].



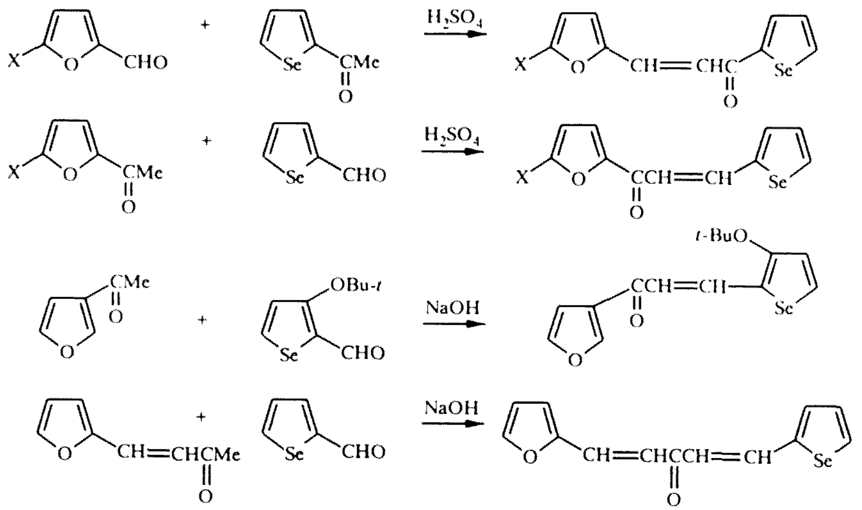
Furoylselenophene can also be obtained with a 46% yield by the acylation of furan with 2-selenophenecarbonyl chloride in carbon disulfide under the influence of anhydrous aluminum chloride with cooling to 5°C. The carbonyl group of the furoylselenophene enters into condensation with hydrazines and is also reduced to a methylene group by lithium aluminum hydride [45].



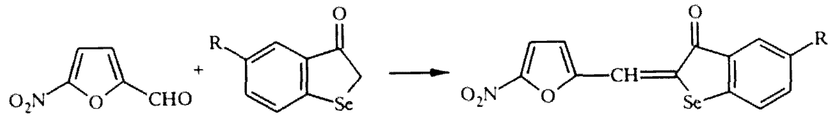
Compounds in which the furan and selenophene rings are separated by a longer carbon chain were obtained by the condensation of various aldehydes and ketones containing furan and selenophene substituents. An unsymmetrical β-diketone is formed with a 70% yield during the reaction of 2-acetylselenophene with methyl pyromucate under the influence of sodium amide [46, 47]. It reacts in turn with formalin in ethanol with piperidine as catalyst. (Condensation does not take place with morpholine.) The yield of 1,3-di(2-furoyl)-1,3-di(2-selenenoyl)propane is small and only amounts to 22.5% [48].



The condensation of 2-acetylselenophene or 2-formylselenophene with derivatives of furfural, 3-formylfuran, or 2-acetylfuran takes place in the presence of both acidic (sulfuric acid) [49] and alkaline catalysts (sodium hydroxide) [50, 51].

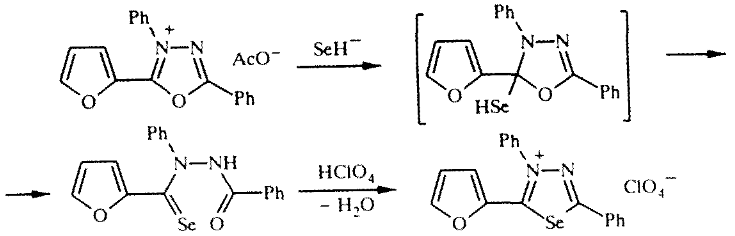


The hydrogen atoms at position 2 of 5-substituted 2,3-dihydrobenzoselenophen-3-ones have adequate mobility, as a result of which these compounds readily react with 5-nitrofurfural [52].

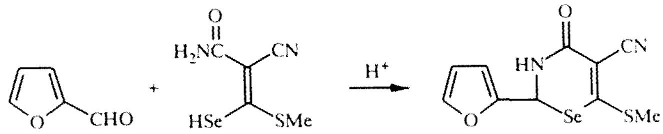


R = H, Me, Cl

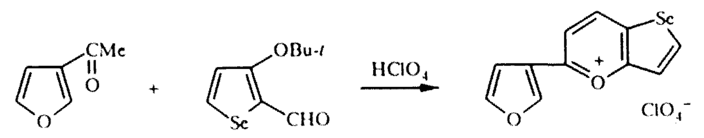
In addition to the furyl-containing derivatives of selenophene discussed above, furan compounds whose molecules contain various selenium-containing heterocycles have also been synthesized [51, 53-55]. Thus, 1,3,4-oxadiazolium salts can easily be converted into 1,3,4-selenadiazolium salts by the action of hydroselenides MSeH on oxadiazolium salts followed by acid cyclodehydration of the intermediates [53, 54].



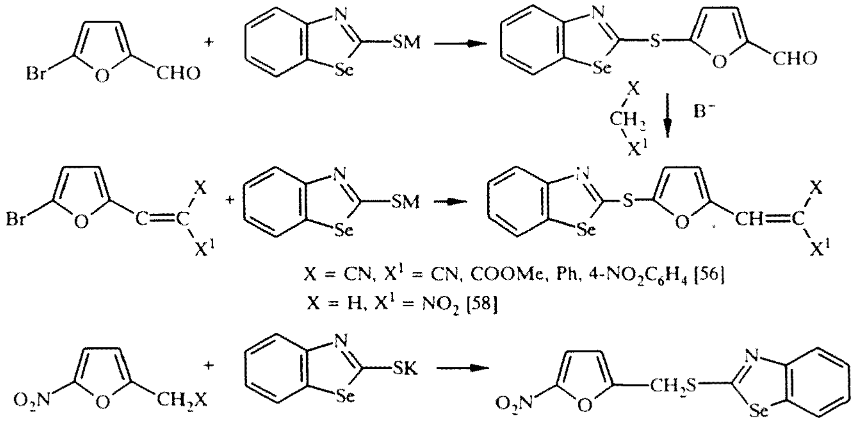
2-Cyano-3-hydroseleno-3-methylacrylamide reacts with furfural in the presence of an acidic catalyst. The yield of the cyclization product (a furyl-containing 1,3-selenazin-4-one) amounts to 72% [55].



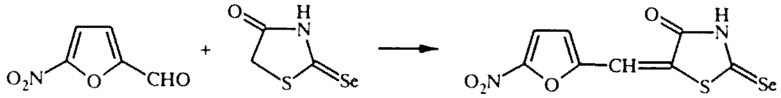
Whereas the condensation of 3-acetylfuran with 2-formyl-3-*tert*-butoxyselenophene in an alkaline medium leads to the formation of a linear product with a very low yield (9%), in the presence of perchloric acid these compounds give the cyclocondensation product with yields of 90% [51].



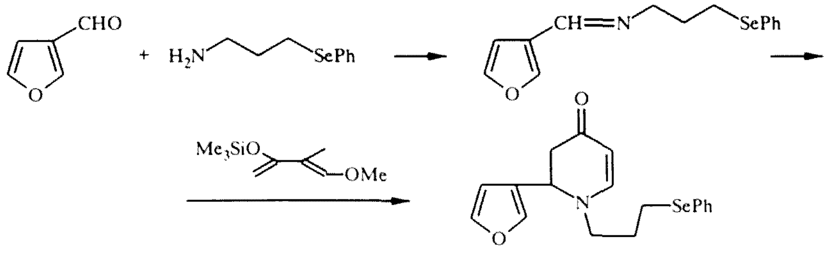
A series of compounds in which the furan ring and the selenium atom are linked by a carbofunctional chain were synthesized. For example, methods were developed for the production of 2-furyl- and 2-furfurylthiobenzoselenazoles [56-58]. Usually, these compounds are formed during the reaction of sodium and potassium 2-benzoselenazolethiolates with bromofurans in ethanol [56] and halogenomethylfurans in aromatic hydrocarbons [57] at room temperature. It was possible to reduce the reaction time from 8 to 3 h and to increase the yield of 2-furfurylthiobenzoselenazoles to 80% by replacing the thiolates by a mixture of 2-benzoselenazolethiol and potassium carbonate [57].


$X = CN$, $X^1 = CN$, COOMe, Ph, 4-$NO_2C_6H_4$ [56]
$X = H$, $X^1 = NO_2$ [58]

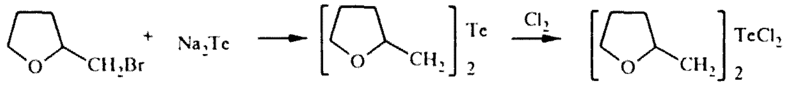
During the condensation of 2-selenoxo-1,3-thiazolidin-4-one with 5-nitrofurfural in glacial acetic acid 2-selenoxo-5-(5-nitrofurfurylidene)-1,3-thiazolidin-4-one was obtained [59].



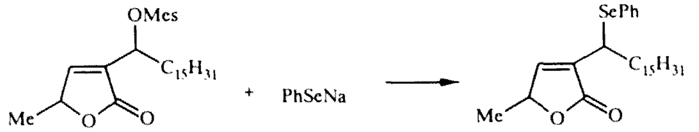
The azomethine base synthesized in the usual way from 3-formylfuran and 3-aminopropyl phenyl selenide enters into the Diels—Alder reaction with 1-methoxy-2-methyl-3-trimethylsilyloxybutadiene as diene. The cyclization product (a derivative of tetrahydropyridinone with a phenylselenopropyl group at the nitrogen atom of the heterocycle) is formed with 72% yield [60].



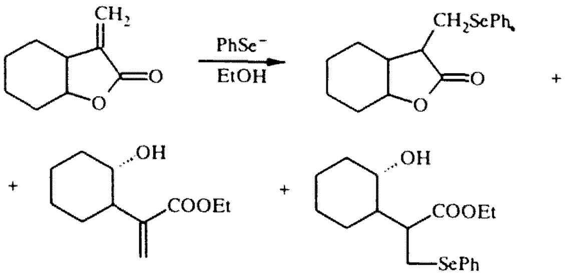
The main method for the synthesis of the tetrahydrofuran derivatives of selenium and tellurium of type (II) involves the cyclization of alkenes in the presence of water [24, 61, 62], unsaturated alcohols [25, 63-69], and acids [70, 71] under the influence of various selenating (N-phenylselenophthalimide, N-phenylselenosuccinimide, PhSeCl, PhSeCN, Ph_2Se_2) and tellurating [TeO_2, $(ArTe{=}O)_2O$] agents. Other methods, such as the substitution of functional groups by a heteroorganic substituent [66, 72] or addition at the methylene group of α-methylenelactones, are used extremely rarely. Thus, in reaction with tetrahydrofurfuryl bromide sodium telluride gives di(tetrahydrofurfuryl) telluride, which can in turn be easily converted into derivatives of tetravalent tellurium by the action of chlorine [66].



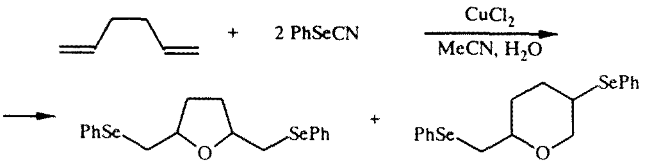
The 2,4,6-trimethylphenoxy group can also be substituted by a phenylselenium group by the action of sodium phenyl selenide in ethanol with cooling to −10°C [72].



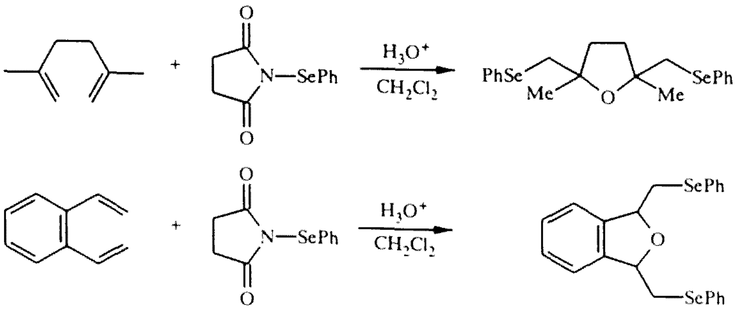
The phenylselenide anion, produced by the treatment of diphenyl diselenide with sodium borohydride in ethanol, adds to the methylene of α-methylenelactone. Apart from the addition product (60%), the reaction mixture also contained products from opening of the lactone ring, but their yields were low (6%) [73].



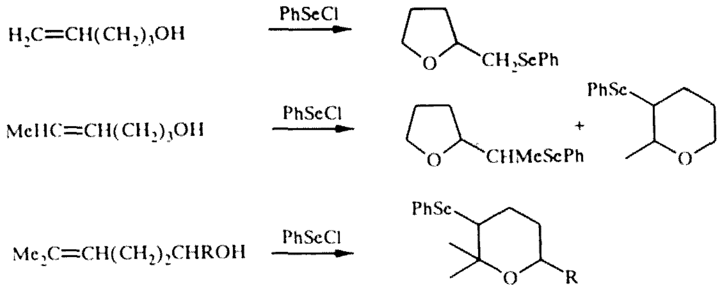
The cyclization of 1,5-hexadiene under the influence of phenyl selenocyanate in a water—acetonitrile medium in the presence of copper(II) chloride leads to the formation of both the tetrahydrofuran derivative and the tetrahydropyran derivative in a ratio of 9:1 and with an overall yield of 84% [61, 62].



Only the tetrahydrofuran derivatives were obtained with yields of 63 and 70% respectively from 2,5-dimethyl-1,5-hexadiene and 1,2-divinylbenzene during treatment with N-phenylselenosuccinimide in methylene chloride in the presence of a 2-3-fold excess of water and an acidic catalyst (e.g., p-toluenesulfonic acid) [24].

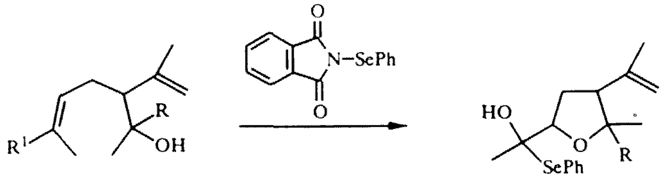


It was possible to realize the cyclization of unsaturated alcohols by means of N-phenylselenophthalimide [25] and phenylselenium chloride [63, 68]. In reaction with phenylselenium chloride 4-alken-1-ols give five- and/or six-membered cyclic ethers, the ratio of which depends on the substituents at the double bond and the carbinol carbon atom [63]. Thus, 4-penten-1-ol only forms a tetrahydrofuran ring, 5-methyl-4-hexen-1-ol and 6-methyl-5-hepten-2-ol form a tetrahydropyran ring, and 4-hexen-1-ol forms a mixture of products of the tetrahydrofuran and tetrahydropyran series.



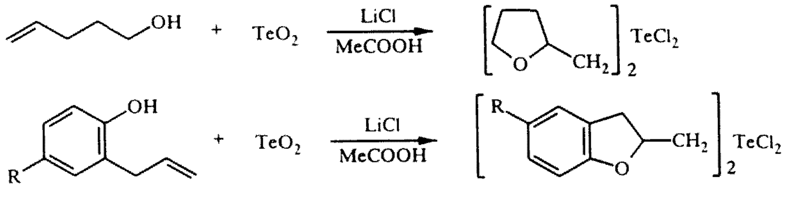
R = H, Me

Unsaturated alcohols containing a 1,5-hexadien-3-ol fragment are converted by the action of N-phenylphthalimide in the presence of a catalyst of acidic type into tetrahydrofuran derivatives, containing a phenylselenomethyl group at position 2, with yields of 58-70% [25].



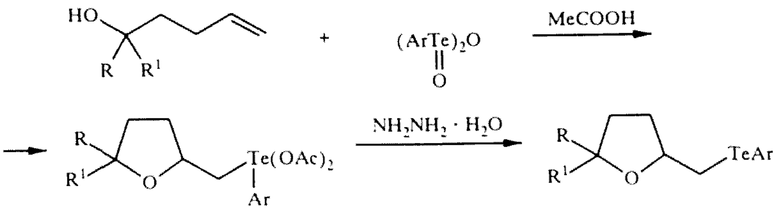
R = $H_2C{=}CH$, R^1 = Me (64%)
R = $H_2C{=}CH$, R^1 = $Me_2C{=}CHCH_2CH_2$ (70%)
R = $HC{\equiv}C$, R^1 = Me (58%)

Tellurium dioxide in a solution of acetic acid containing lithium chloride gives rise to the cyclization of 4-propen-1-ol. The yield of di(tetrahydrofurfuryl)dichlorotellurium amounts to 58% [66]. 2-Allylphenols also enter into a similar reaction [66].



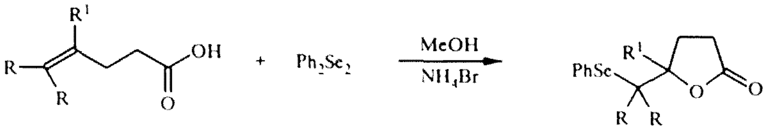
R = H, Me, Cl

The treatment of hydroxyolefins with arenetellurinic anhydrides [$(ArTeO)_2O$, Ar = Ph, *p*-$MeOC_6H_4$, α-$C_{10}H_7$] in acetic acid at boiling point for 15 h leads to the formation of tetrahydrofuran derivatives with a functional tellurium group [$Ar(AcO)_2Te$]. These compounds are hygroscopic and unstable, and they were therefore isolated in the form of tellurides with yields of 70-90% after reduction with hydrazine hydrate in ethanol [64, 65].



R = R^1 = H, RR^1 = $(CH_2)_5$, $(CH_2)_6$

γ-Lactones with phenylselenomethyl groups at the γ position were obtained with 60-70% yields by the electrolysis of unsaturated carboxylic acids and diphenyl diselenide in a methanol solution of ammonium bromide. A graphite rod was used as anode, and the cathode was of copper foil [70].

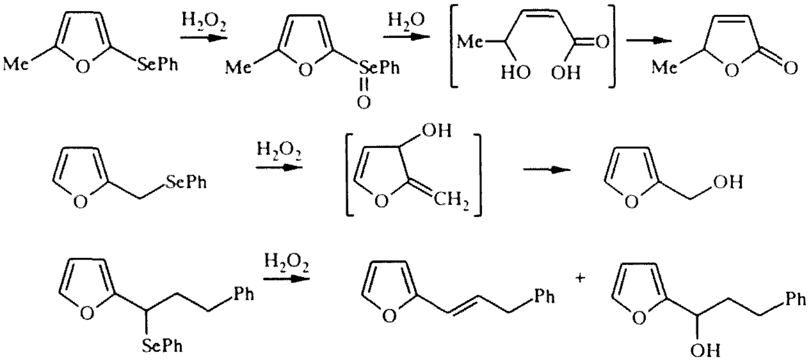


$R = R^1 = H$; $R = H$, $R^1 = Me$; $R = Me$, $R^1 = H$

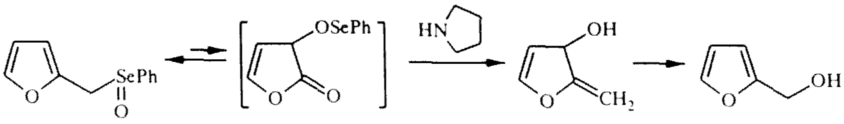
1.3. Chemical Properties

The most widely employed reaction in the series of furyl and tetrahydrofuryl selenides is deselenation. Cleavage of the Se—C bond has usually been achieved with 30% hydrogen peroxide [16, 30, 32, 33, 72, 73], and *m*-chloroperbenzoic acid [31], sodium periodate [31], and tributylstannane [38, 74] have also been used.

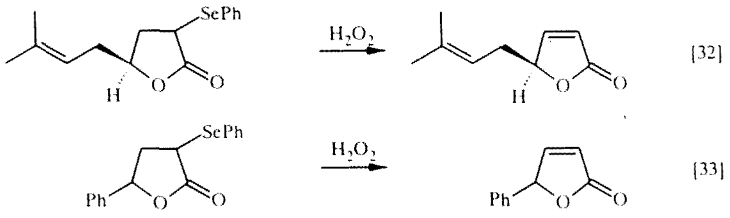
During the oxidation of 2-phenylseleno-5-methylfuran with hydrogen peroxide the only reaction product was 5-methyl-2-furanone (74%). Oxidation most likely takes place through the selenoxide, which during attack by water gives the unstable hydroxy acid, and the latter undergoes cyclization to the furanone [16]. For 2-phenylselenomethylfuran under analogous conditions [2,3]-sigmatropic rearrangement, leading to furfuryl alcohol, is possible. The action of hydrogen peroxide on 1-(2-furyl)-1-phenylseleno-3-phenylpropane gave a mixture of products, i.e., 1-(2-furyl)-2-benzylethylene and a derivative of furfuryl alcohol, produced also as a result of a [2,3]-sigmatropic rearrangement [16].

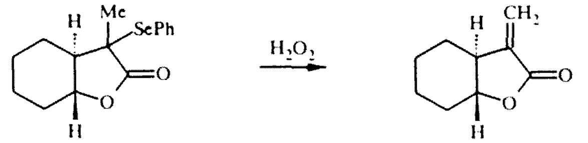


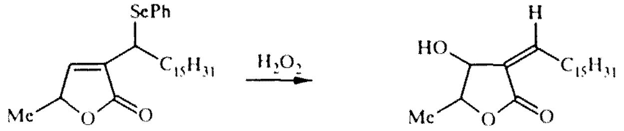
In order to obtain evidence for the possibility of such a rearrangement in furfuryl phenyl selenoxide its thermodynamic properties were investigated by NMR spectroscopy [75]. Although the selenoxide was the only structure detected by this method, the authors [75] consider that there is a rapid equilibrium with the product of the [2,3]-sigmatropic rearrangement, since an alcohol is formed in the reaction with pyrrolidine.



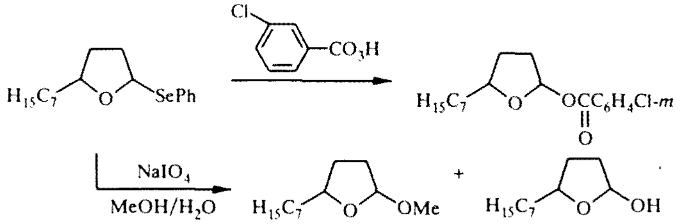
Removal of the phenylseleno group has very often been used for the synthesis of various natural compounds, such as pheromones [32] and substances isolated from higher plants [72].



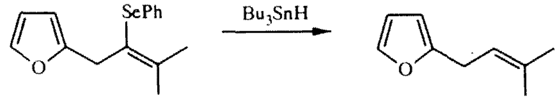

[30]


[72]

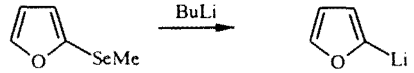
The formation of 2-hexyl-2,3-dihydrofuran was not observed during the oxidation of 2-hexyl-5-phenylselenotetrahydrofuran with *m*-chloroperbenzoic acid or sodium perchlorate in a mixture of methanol and water [31]. Tetrahydrofuryl *m*-chlorobenzoate was obtained in the first case, and an 11:9 mixture of methoxy- and hydroxytetrahydrofurans was obtained in the second [31].



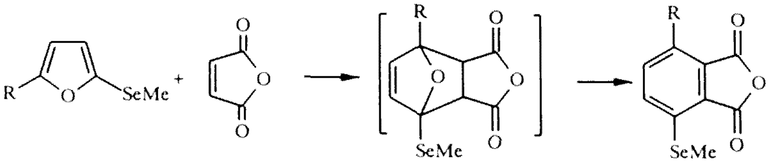
1-(2-Furyl)-2-phenylseleno-3-methylbut-2-ene is reduced by tributylstannane in the presence of azobisisobutyronitrile to 1-(2-furyl)-3-methylbut-2-ene, the yield of which amounts to 70% [38].



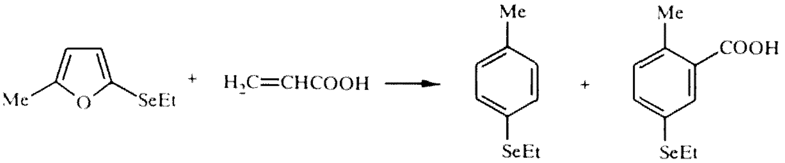
Cleavage of the Se—C_{furyl} bond is also observed in the reaction with butyllithium. Attempts to metallate position 5 of the furan ring of 2-methylselenofuran were unsuccessful, and the only reaction product was 2-furyllithium [9, 76].



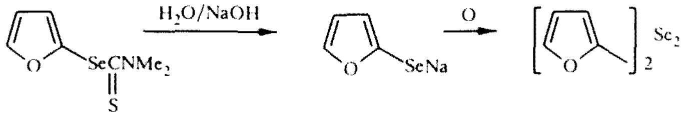
There are at present no published data on the introduction of functional groups into the furan ring of furyl selenides by electrophilic substitution. The furan ring was transformed by a diene synthesis. During the reaction of 2-methylselenofuran and 5-methyl-2-methylselenofuran with maleic anhydride the derivatives of phthalic anhydride were obtained with yields of 42 and 46% respectively [9, 76]. 5-Methyl-2-methylselenofuran proved considerably less reactive toward acrylic acid. Moreover, the reaction was nonselective and gave a mixture of two products (total yield ~20%) [77].



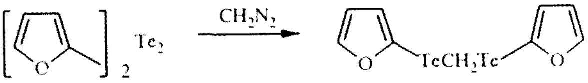
R = H, Me



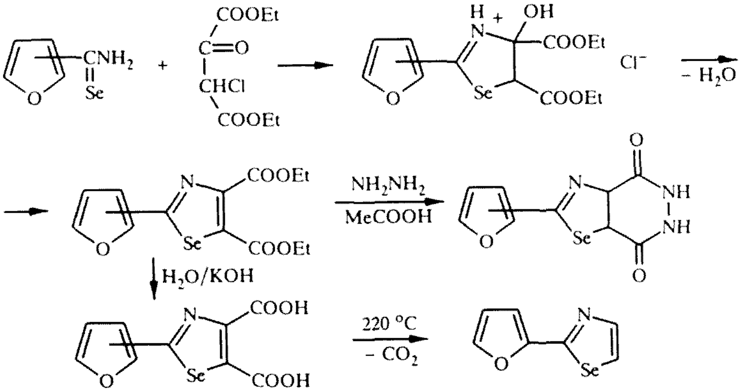
The chemical transformations of the substituents at the elements in furyl selenides and furyl tellurides have also been investigated little. 2-Furyl selenothiocarbamate is hydrolyzed in an alkaline medium with the formation of sodium 2-furyl selenide, which is transformed during oxidation into di(2-furyl) diselenide with a yield of 70% [10].



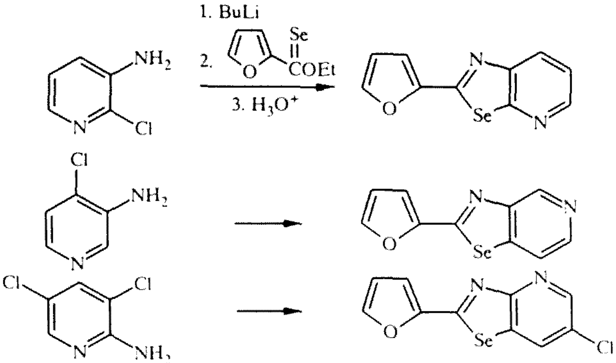
The carbene produced from diazomethane is capable of entering at the Te—Te bond of di(2-furyl) ditelluride at 0°C [78].



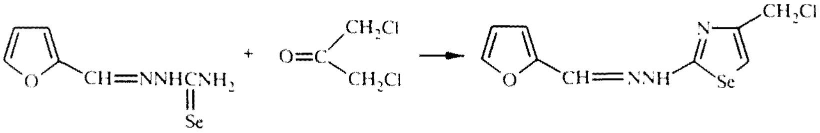
A series of furan derivatives containing a selenoxo group were used for the production of polyheterocyclic compounds [79-84]. Thus, the amides of 2- and 3-furancarboselenoic acids enter into condensation with diethyl oxo(chloro)succinate in acetone with the formation of 2-furylselenazoles [79-81].



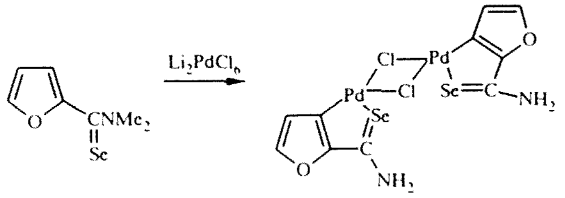
Ethyl 2-furancarboselenoate gives cyclization products with the lithium derivatives of 2-chloro-3-aminopyridine, 3-amino-4-chloropyridine, and 2-amino-3,5-dichloropyridine, which were obtained by treating the pyridines with butyllithium in tetrahydrofuran [82]. The yield of the 2-(2-furyl)selenazolopyridines amounted to 51-58%.



Furfural selenosemicarbazone enters into reaction with symmetrical dichloroacetone. In this case, as in the previously examined cases, cyclocondensation occurs, and a selenazole derivative is formed [83].



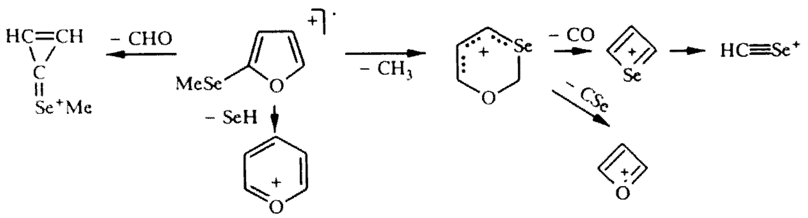
The reactions of 2- and 3-furancarboselenoamides with Li_2PdCl_4 in methanol at room temperature give chelates, in which the palladium atom is coordinated with the selenoxo group and the carbon atom of the furan ring at position 3 for the 2-substituted amide and at position 2 for the 3-isomer [84].



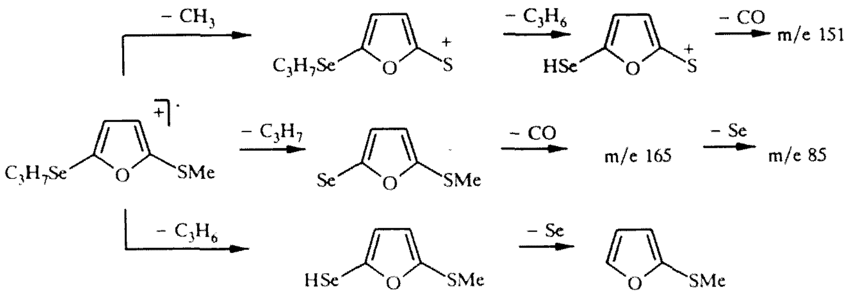
1.4. Physicochemical Properties

There have not been many physicochemical investigations into the structural features of furyl selenides. An analysis was made of the mass-spectrometric dissociation of 2-methylselenofuran [85] and 2-furfurylselenophene [86] and the UV spectra and dipole moments of 2-phenylselenopheno[2,3-*b*]furan [87] and 2-[(2-furoyl)vinyl]selenophene [88].

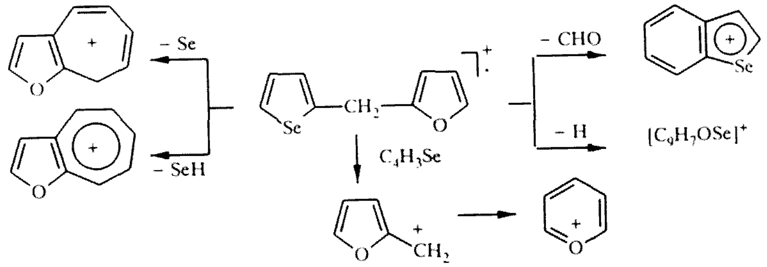
Removal of the methyl group is observed initially in the mass spectrum of 2-methylselenofuran. Concurrent elimination of CO and CSe then occurs, and the loss of CO predominates. The ion most characteristic of the compound is formed during the elimination of SeH from the molecular ion [85].



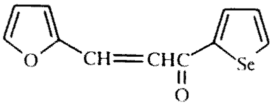
The dissociation of 2-methylthio-5-propylselenofuran during electron impact takes place according to the following scheme [85]:

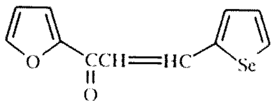


For 2-furfurylselenophene, the main process leads to the formation of the M − 29 ion. It can be supposed that the C—O bond is cleaved first, the formyl fragment is eliminated, and the benzoselenophene ion, which is a source of ions with smaller masses, is formed. In addition, the elimination of the selenophene ring and the resultant formation of a pyrylium ion are observed, and Se and SeH are also eliminated.



In the UV spectrum of 2-phenylselenopheno[2,3-*b*] the band of the $\pi-\pi^*$ transition is distinguished by a steep and high ascent typical of planar systems. In the opinion of these authors [87], therefore, the phenyl substituent is either coplanar with the bicycle or oscillates in a small range of angles. In the IR spectra the absorption frequency of the carbonyl stretching vibration ν_{CO} is identical for the two chalcones (ν_{CO} = 1657 cm^{-1}), while the experimental values of the dipole moments are 3.44 and 3.23 D respectively [88].

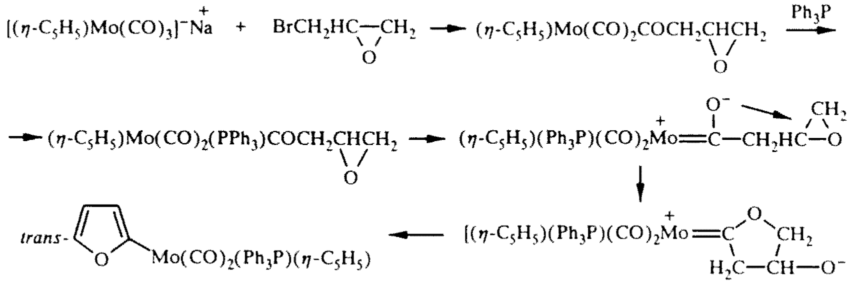




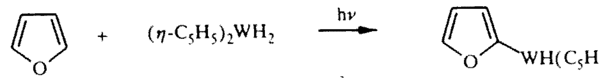
2. DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

2.1. Synthesis

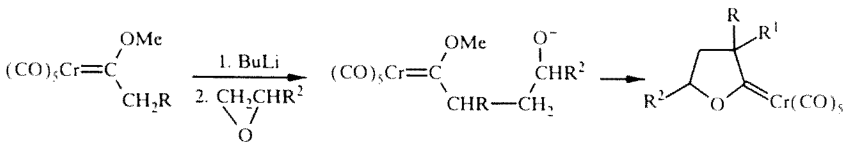
Compounds with a C_{furyl}—Cr bond are unknown; one compound with a C_{furyl}—Mo bond and one with a C_{furyl}—W bond have been synthesized. The first compound, in which the molybdenum atom is attached to the furan ring, was obtained by an original method in the reaction of sodium (η-cyclopentadienyl)tricarbonylmolybdate with bromomethyloxirane in the presence of an excess of triphenylphosphine, which performs an important role in the formation of the furan ring [89]. If the reaction is conducted without the triphenylphosphine, the complex $(\eta\text{-}C_5H_5)Mo(CO)_2CO—O—CH_2CH═CH_2$, in which the molybdenum atom is π-bonded with the double bond of the allyl group, is formed. With an excess of triphenylphosphine the furan complex of molybdenum was obtained with a yield of 20% according to the following scheme [89]:



During irradiation of the cyclopentadiene complex of tungsten $(\eta\text{-}C_5H_5)_2WH_2$ in furan, insertion of the tungsten complex $W(C_5H_5\text{-}\eta)_2$ at the C—H bond with the formation of a furan derivative of tungsten was observed [90].



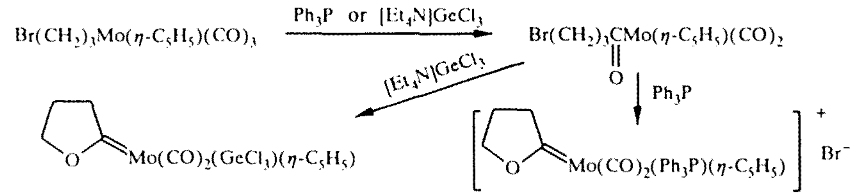
The cyclization of the lithium derivatives of (alkylmethoxycarbene)pentacarbonylchromium with epoxides was used for the synthesis of 2-oxacyclopentylidene complexes of chromium [91, 92]. Initially, the anion of the lithium derivative of the complex attacks the oxirane molecule, and this is followed by elimination of the methoxide anion and cyclization [92].



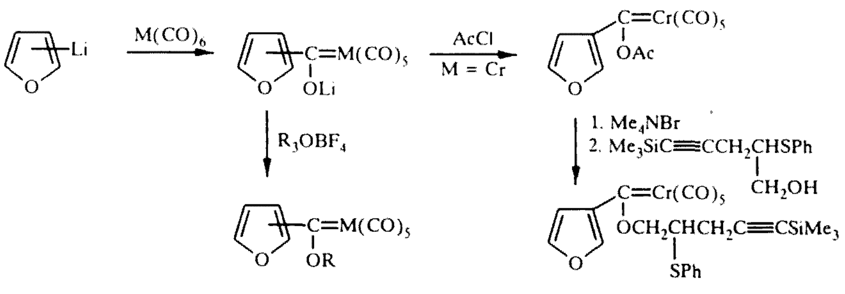
R = R^1 = R^2 = H (50%); R = R^1 = H, R^2 = Me (38%); R = Me, R^1 = R^2 = H (18%)

In the reaction of the (ethylmethoxycarbene)pentacarbonylchromium anion with ethylene oxide, the complex with R = Me, R^1 = CH_2CH_2OH, and R^2 = H (42%) is formed in addition to the usual product with R = Me and R^1 = R^2 = H.

The analogous compounds of molybdenum were obtained as a result of the action of triphenylphosphine [93] and the germanium-containing salt $[Et_4N]GeCl_3$ [94] on cyclopentadienyl(tricarbonyl)(3-bromopropyl)molybdenum. In both cases the acyl derivative was formed initially, and its oxygen atom attacked the carbon atom at the γ position intramolecularly with the elimination of a bromide anion.

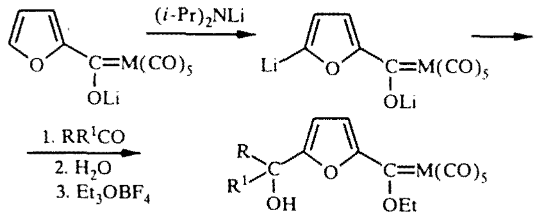


The lithium method used for the synthesis of (pentacarbonyl)furylcarbenium complexes of chromium [95, 96], molybdenum [97, 98], and tungsten [96, 98] involved the reaction of 2-furyllithium [96-98] and 3-furyllithium [95, 97] with hexacarbonyl complexes $M(CO)_6$ (M = Cr, Mo, W). Addition of the furyllithium to one of the carbonyl groups with the formation of an anionic complex was observed initially. The complex is easily converted into the corresponding alkoxy derivatives with trialkoxyoxonium tetrafluoroborate [96-98] and into acetoxy derivatives by treatment with acetyl chloride [95].



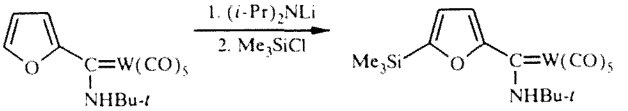
M = Cr, Mo, W; R = Me, Et

In addition, the anionic complexes of chromium and tungsten are stable to the action of strong bases. It was, therefore, possible to metallate them at position 5 of the furan ring with lithium diisopropylamide [96]. Further treatment with aldehydes or ketones, water, and triethyloxonium tetrafluoroborate gave 5-substituted furan derivatives.

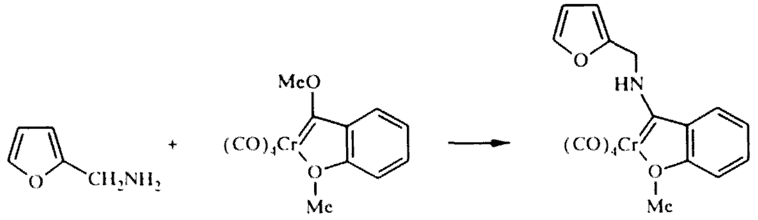


M = Cr, R = Ph, R^1 = H (69%); M = W, R = i-Pr, R^1 = H (79%), $RR^1 = (CH_2)_5$ (27%)

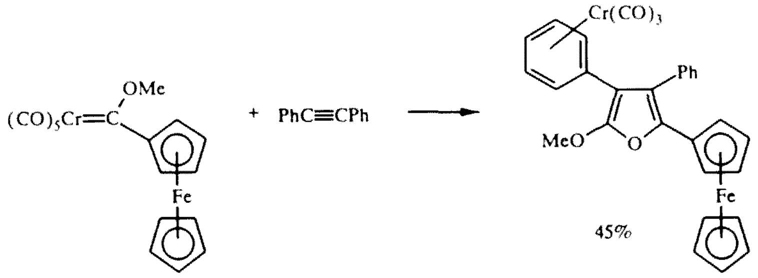
The product from silylation of the furan ring at position 5 was obtained with a yield of 22% from the aminocarbene complex of tungsten in reaction with lithium diisopropylamide in the presence of trimethylchlorosilane [96].



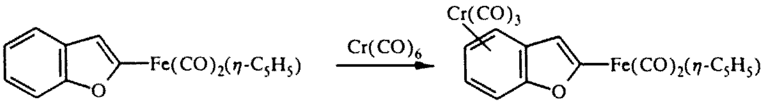
The ammonolysis of the (2-methoxyphenyl)methoxycarbenium complex of chromium by furfurylamine at low temperature takes place with substitution of the methoxy group. The chromium atom and furan ring in the reaction product are separated by a carbofunctional chain. According to x-ray crystallographic analysis, the oxygen atom in the furfurylaminocarbene complex is not coordinated with the chromium atom (r Cr···O = 3.917 Å) [99].



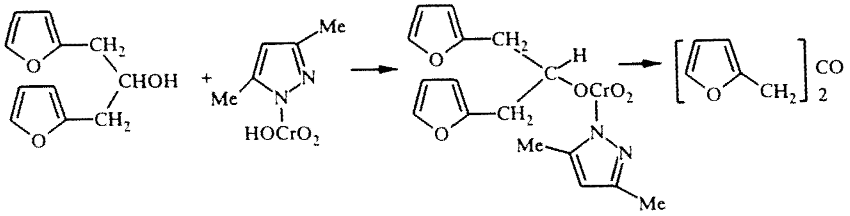
In addition to the furylcarbene complexes of chromium, molybdenum, and tungsten, a series of chromium tricarbonyl complexes [100-103] of arylfurans and benzofurans were obtained. Pentacarbonyl[ferrocenyl(methoxy)carbene]chromium reacts with diphenylacetylene in dibutyl ether after heating for 4 h (80°C) with the elimination of carbon monoxide and the formation of a furan ring [100].



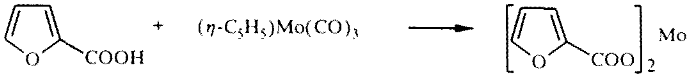
The reaction of hexacarbonylchromium $Cr(CO)_6$ with the benzofuran derivatives of cyclopentadienyldicarbonyliron gave a high yield of a complex in which the heterocycle was linked to the iron atom by a σ bond, while the chromium atom was π-coordinated with the benzene ring of the benzofuran [102].



Furan compounds in which the chromium or molybdenum atom is linked to the oxygen atom have been studied very little [104-106]. Thus, the chromium derivative of difurfurylcarbinol, obtained by treatment of the respective alcohol with the 3,5-dimethylpyrazole complex of chromium, is an intermediate in the preparation of difurfuryl ketone [106].



The chromium and molybdenum salts of pyromucic acid were also synthesized [104, 105]. In the reaction of (cyclopentadienyl)tricarbonylmolybdenum with pyromucic acid in boiling toluene it was not possible to substitute the carbonyl groups selectively, since removal of the cyclopentadienyl group with the formation of molybdenum di(furancarboxylate) was also observed.



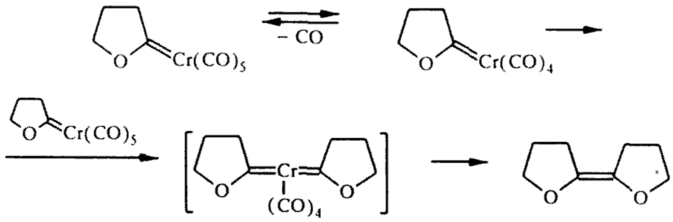
Chromium 5-*tert*-butylpyromucate was used as catalyst during the cleavage of an epoxide ring by acyloxysilanes [107-109].

Various furyl-containing compounds, such as 1-(2-furyl)-3-phenyl-1,3-propanedione [110], furfural thiosemicarbazones and semicarbazones [111], 2-(2-furyl)benzothiazole [112], and furaldazine [113], act as ligands in chelate compounds of chromium [110, 111], molybdenum [112-113], and tungsten [113]. They are usually obtained in the reaction of the furan derivatives with salts of the metals.

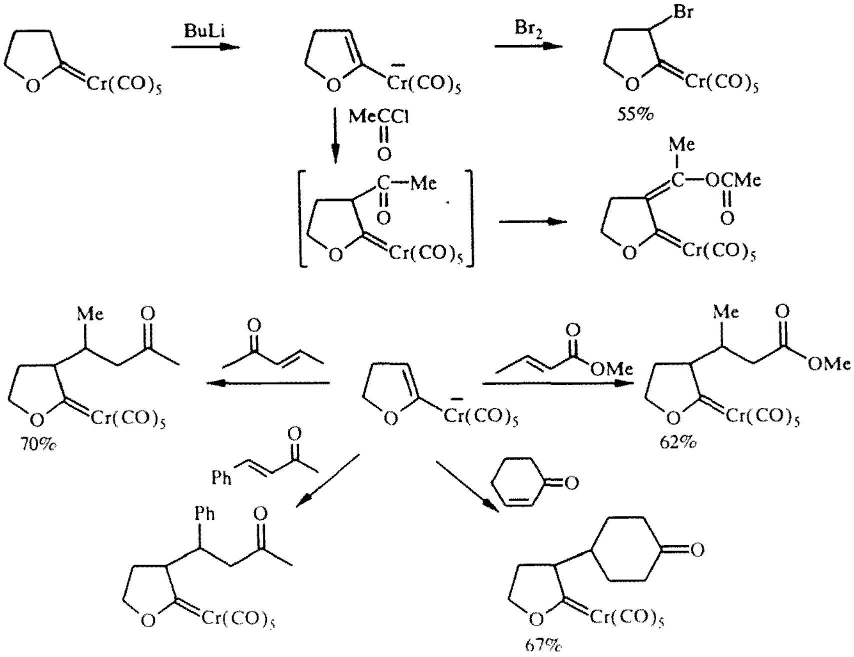
2.2. Chemical Properties

In the series of furan derivatives of elements of the chromium subgroup, the chemical transformations of two types of compounds have been investigated, i.e., (2-oxacyclopentylidene)pentacarbonylchromium [114, 115] and furylcarbene complexes of chromium [101, 116-119] and tungsten [120, 121].

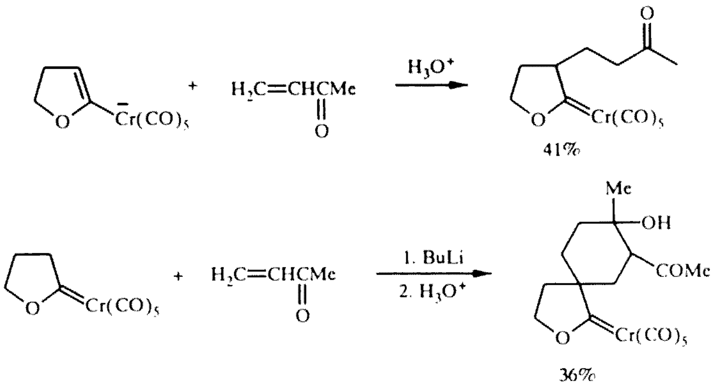
The thermolysis of (2-oxacyclopentylidene)pentacarbonylchromium in decalin at 139°C leads to the formation of a dimer (and not cyclobutanone), indicating that the reaction takes place by a bimolecular mechanism and not through the free carbene [114]. The decomposition of the complex in the presence of pyridine leads to a quantitative yield of dihydrofuran [114].



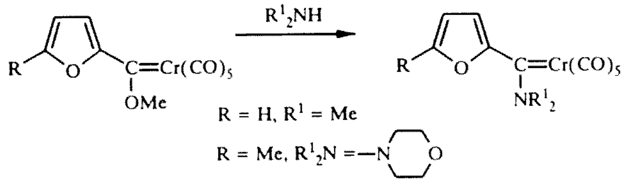
When treated with an equimolar amount of butyllithium at −78°C, (2-oxacyclopentylidene)pentacarbonylchromium forms an anion, which enters into reaction with bromine, acetyl chloride, and α,β-unsaturated carbonyl compounds. During bromination the bromocarbene complex of chromium was obtained with a 55% yield; acylation led to a 1:1 mixture of the *Z* and *E* isomers, while the reactions with 2-cyclohexenone, *trans*-3-penten-2-one, *trans*-1-phenylbuten-3-one, and methyl crotonate gave diastereomeric mixtures of the monoalkylated adducts [115].



In reaction with methyl vinyl ketone, the anion of (2-oxacyclopentylidene)pentacarbonylchromium only gives the monoalkylated adduct with a yield of 41%. However, if the reaction is conducted in the presence of a catalytic amount of butyllithium with an excess of methyl vinyl ketone, the dialkylation product is formed initially and then undergoes intramolecular aldol condensation [115].



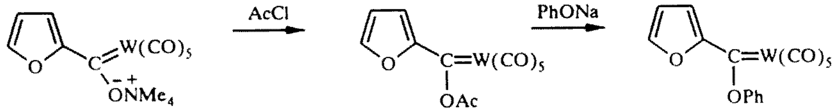
In the series of furylcarbenium complexes of chromium and tungsten containing a functional group together with the furyl substituent at the carbenium carbon, two types of transformations were studied, i.e., substitution of the functional group [116, 120, 121] and condensation with various acetylene compounds [101, 116-119]. The methoxy group in pentacarbonyl[(2-furyl)methoxycarbene]chromium can be substituted by an amino group by the action of an excess of diethylamine or morpholine with strong cooling, and the yield of the aminocarbene complexes amounts to 85% [116].



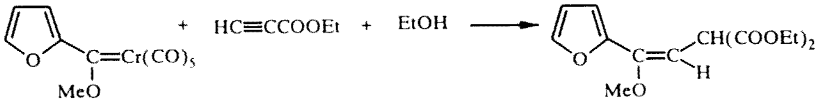
R = H, R^1 = Me

R = Me, R^1_2N = morpholino

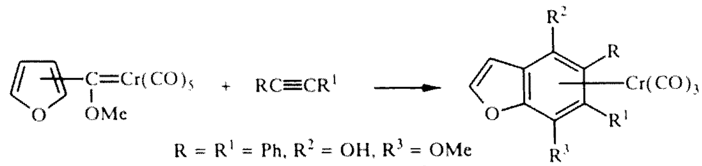
The tetramethylammonium salt of the furylcarbene complex of tungsten is acylated by acetyl chloride with the formation of pentacarbonyl[(2-furyl)acetoxycarbene]tungsten [120]. When treated with sodium phenolate in ether, the product in turn gives pentacarbonyl[(2-furyl)phenoxycarbene]tungsten [121]. Both reactions were conducted with cooling to −5 to −20°C.



The (2-furyl)methoxycarbene complex of chromium reacts with ethyl propiolate in the presence of ethanol when heated in tetrahydrofuran and forms the furylvinyl derivative of diethyl malonate as a mixture of two isomers (1:1.2) with a total yield of 80% [118].



The reaction of the 2-furylcarbene complex of chromium and its 3-isomer with diphenylacetylene and 1-pentyne leads to cyclization to the benzofuran derivatives, in which the benzene ring is coordinated with the chromium tricarbonyl fragment. The reaction is stereoselective, and the yield of the cyclization products from the 2-phenylcarbene complex is small (19-23%). In the reaction of pentacarbonyl[(3-furyl)methoxycarbene]chromium with diphenylacetylene, the yield is increased to 62% [101].

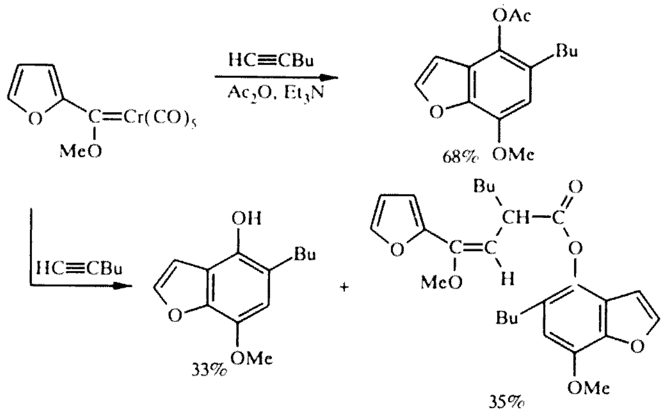


R = R^1 = Ph, R^2 = OH, R^3 = OMe

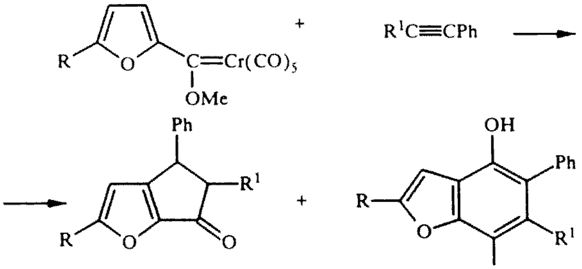
R = Pr, R^1 = H, R^2 = OH, R^3 = OMe

R = R^1 = Ph, R^2 = OMe, R^3 = OH

The condensation of 1-hexyne with pentacarbonyl[(2-furyl)methoxycarbene]chromium in the presence of acetic anhydride and triethylamine in tetrahydrofuran also takes place selectively with the formation of 4-acetyl-5-butyl-7-methoxybenzofuran with a yield of 68%. If the reaction is carried out without the acetic anhydride, a mixture of two products is formed [117].

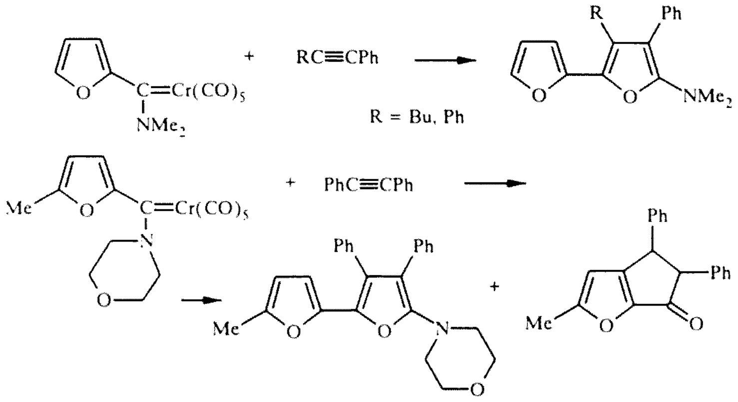


The cyclization of the methoxy- and aminocarbene complexes of chromium with disubstituted acetylenes in dimethylformamide, heated to 120°C, takes place in a different way. In the case of the methoxycarbenes, the main products are compounds in which the furan ring is condensed with the cyclopentanone ring and are produced in the form of mixtures of *cis* and *trans* isomers. In addition, small amounts (8-9%) of benzofurans are formed [116].



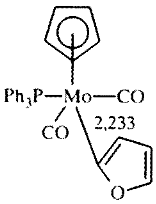
R = H, R^1 = Ph (cis - 24%, trans - 37%)
R = Me, R^1 = Ph (cis - 24%, trans - 32%)
R = Me, R^1 = Bu (cis - 14%, trans - 37%)

With diphenylacetylene and phenylbutylacetylene, the (2-furyl)dimethylaminocarbene complex of chromium gives small yields of difuran products (21-44%). If the dimethylamino group is replaced by morpholine and a methyl group is introduced at position 5 of the furan ring, the reaction with diphenylacetylene is not so well-defined; a 1:1 mixture of *cis* and *trans* isomers of cyclopentanone was obtained with a yield of 27% in addition to the bifuran [116].

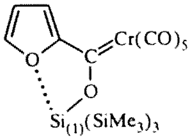


2.3. Molecular Structure of the Furan Complexes of Chromium and Tungsten

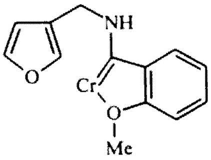
The stereochemical structure of some complexes of chromium [99, 100, 122] and molybdenum [89] was studied by x-ray crystallographic analysis. In dicarbonyl(cyclopentadienyl)(triphenylphosphine)(2-furyl)molybdenum the metal atom is directly attached to the furan ring, and the length of the C_{furyl}—Mo bond is 2.233 Å. The lengths of the C(2)—C(3), C(3)—C(4), and C(4)—C(5) bonds in the furan are 1.331, 1.141, and 1.331 Å respectively [89].



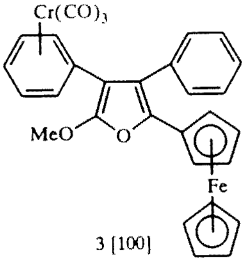
The structure of various types of chromium complexes was investigated.



1 [122]



2 [99]



3 [100]

In the first complex, the structure of which was discussed in the review [4], the chromium atom does not interact with the oxygen atom of the furan ring on account of the fact that the latter is coordinated with the silicon atom [rO···Si(1) = 2.92 Å] [122]. In the furfurylamine derivative (2) the O_{furan}···Cr distance is 3.917 Å, which is also inconsistent with coordination [99].

The plane of the furan ring in [3-(2-methoxy-4-phenyl-5-ferrocenylfuryl)benzene]tricarbonylchromium (3) forms a dihedral angle of 17.7° with the benzene ring coordinated with the chromium and 80.2° with the uncoordinated ring [100].

The presented data show that furan and tetrahydrofuryl selenides are suitable models for study of the effect of the heterocycle on cleavage of the C—Se bond and can also be used for the synthesis of various natural compounds.

The derivatives of chromium, molybdenum, and tungsten have been studied considerably less. However, the obtained results demonstrate the expediency of further investigation into the effect of coordination with the furan ring on the reactivity of these complexes.

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