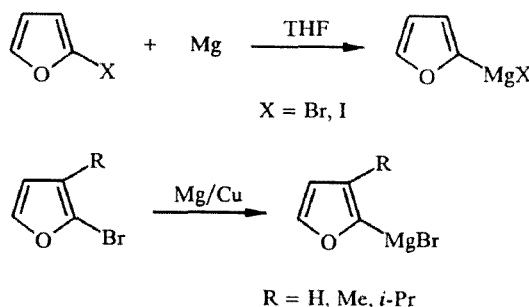


FURAN DERIVATIVES OF GROUP II ELEMENTS (REVIEW)

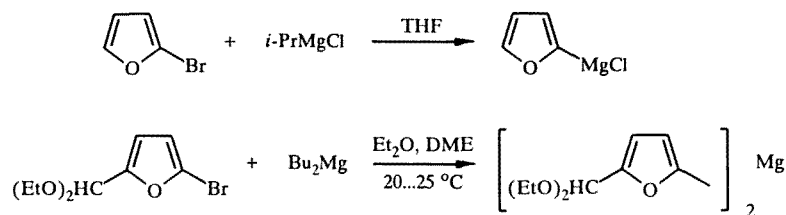
É. Lukevits and O. A. Pudova

1. ORGANOMAGNESIUM DERIVATIVES

Compared with lithium derivatives in which the metal is directly attached to a furan ring [1], magnesium compounds of such a type have been studied to a significantly lesser degree. The halogen atom in 2-chlorofuran [2], 2-bromofuran [2], 2,4,5-triaryl-3-bromofurans [3], and 2-diethoxymethyl-5-bromofuran [4] is unreactive, and these compounds do not react with magnesium. It was possible to obtain 2-furylmagnesium bromide [2, 6-8] in the reaction of 2-bromofuran with a copper – magnesium alloy [2, 7, 8] and by conducting the reaction in THF [6]. 2-Iodofuran has higher reactivity and reacts with magnesium without activation [9].



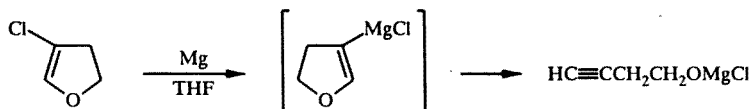
Exchange between bromofurans and alkylmagnesium halides was used for the synthesis of organomagnesium compounds [4, 10]. 2-Furylmagnesium chloride [10] and also a furylmagnesium compound with an acetal group in the ring [4] were obtained by this method.



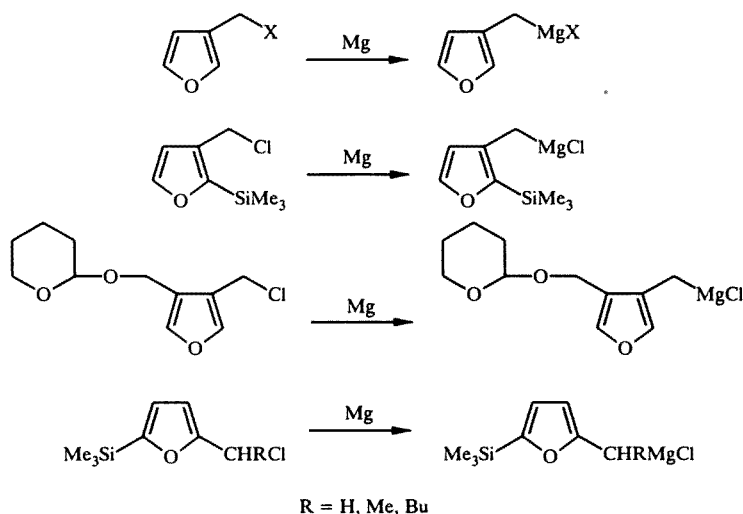
The yields of the magnesium derivatives of furan obtained by this method are fairly low, to judge from the products of the further transformations. For example, the yield of 5-carboxyfurfural after the treatment of di(2-diethoxymethyl-5-furyl)magnesium with carbon dioxide and hydrolysis was 73% [4].

Latvian Institute of Organic Synthesis, Riga LV-1006. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 4, pp. 474-495, April, 1995. Original article submitted March 3, 1995.

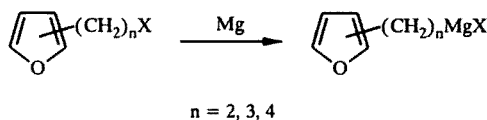
It was not possible to obtain a Grignard reagent from 4-chloro-2,3-dihydrofuran on account of ring opening and the formation of an acetylene derivative [6].



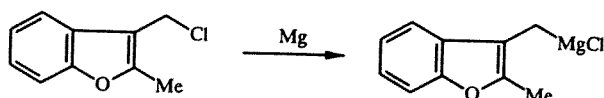
Organomagnesium compounds in which the metal atom and the furan ring are separated by one, two, or three methylene groups are more widely used in synthesis, particularly for the production of natural compounds [11-33]. Not all compounds of this series were obtained. Whereas 3-furylmethylmagnesium chloride [11-17] and bromide [18-25] are formed easily and with high yields from the corresponding halogenomethyl derivatives with slight cooling (to 0°C) in ether and THF, it was not possible to obtain a Grignard reagent from furfuryl chloride on account of its increased lability. It was, however, established [26] that the introduction of a trimethylsilyl group at position 5 of furfuryl chloride had a stabilizing effect, and 5-trimethylsilylfurfurylmagnesium chloride was synthesized in the traditional way in THF [26].



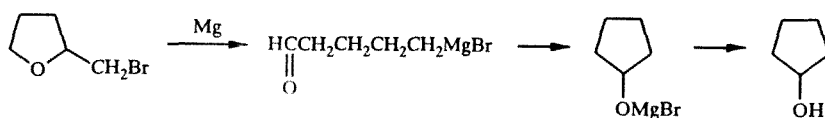
A similar method was used to obtain 2- and 3-furylethyl-, furylpropyl-, and furylbutylmagnesium halides by the action of magnesium on halogenoalkylfurans [27-32].



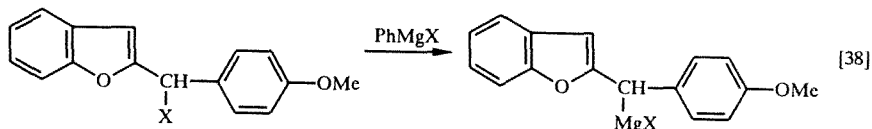
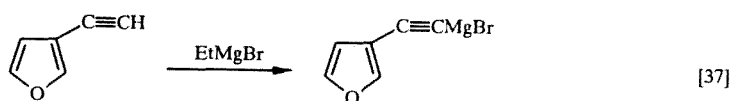
A Grignard reagent was obtained with an 80% yield from 2-methyl-3-chloromethylbenzofuran [33].



Tetrahydrofurfuryl bromide undergoes cleavage at the C–O bond of the heterocycle under the influence of magnesium in ether [34]. Only compounds of the tetrahydrofuran series in which the halogen atom is separated from the ring by three or more methylene groups form Grignard reagents [35, 36].

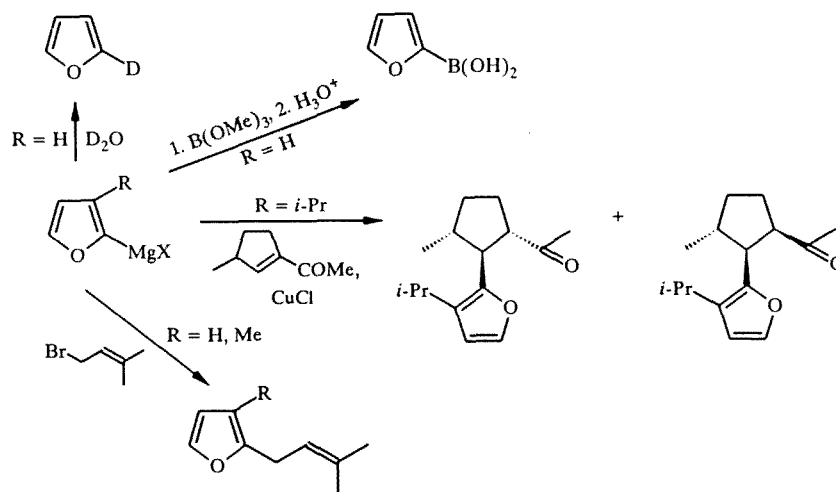


Some organomagnesium compounds of furan containing the metal in a side chain were obtained by substitution of the mobile hydrogen [37] or halogen atom by the MgX group during treatment with alkyl- and arylmagnesium halides [38].



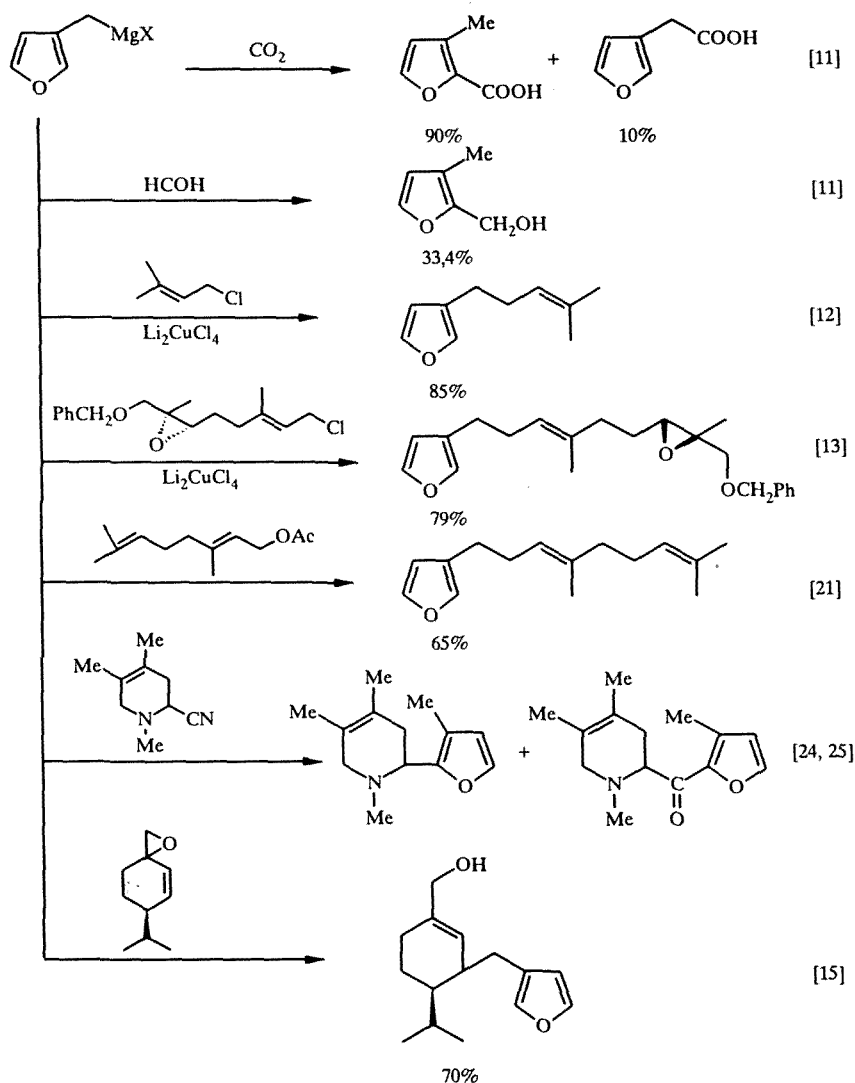
In addition to compounds with a C–Mg bond, the reaction of various functional derivatives of furan (aldehydes, ketones, acids, nitriles, etc.) with Grignard reagents RMgX (R = alkyl, vinyl, ethynyl, phenyl) gave derivatives with O–Mg and N–Mg bonds. As a rule, these compounds were only intermediate products in the synthesis of furan compounds [39-49].

Some chemical transformations of 2-furylmagnesium halides were studied. These included the reactions with deuterated water [10], alkenyl bromides [7], unsaturated ketones [8], and trimethyl borate [9]. 2,5-Diphenyl-3-furylmagnesium bromide reacts with benzoic anhydride with the formation of 2,5-diphenyl-3-benzoylfuran [50].

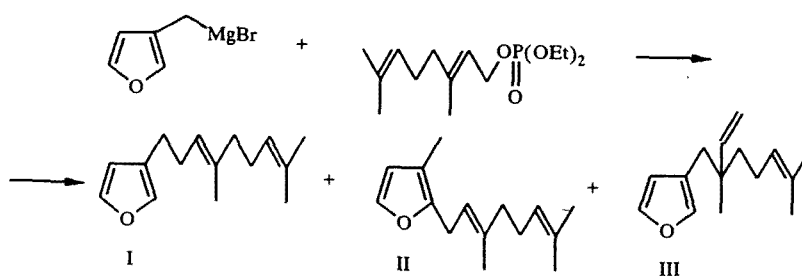


Di(2-diethoxymethyl-5-furyl)magnesium proved inactive in reactions with benzaldehyde and benzonitrile, but it reacted readily with carbon dioxide and was transformed by reaction with ferric chloride into 5,5'-bisfurfural [4].

Of the furylalkylmagnesium halides the properties of (3-furylmethyl)magnesium halides have been most widely investigated [11-26].

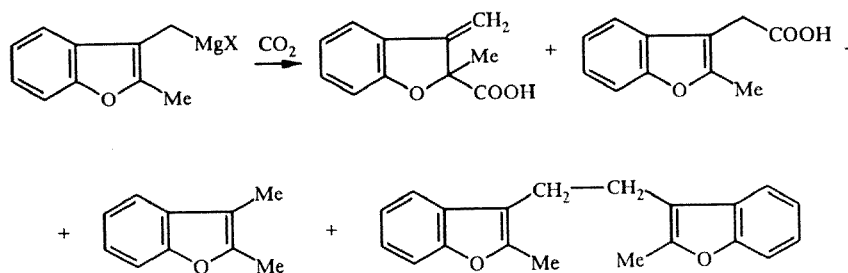


The carbonylation of (3-furylmethyl)magnesium chloride takes place in an untraditional manner [11]. The expected 3-furylacetic acid is only a side product, and 3-methyl-2-furancarboxylic acid is formed with a yield of 90%. Analogous effects are also observed in the reaction with formaldehyde [11], nitrile [23, 25], and also in the noncatalytic reaction with geranyl diethyl phosphate [22].

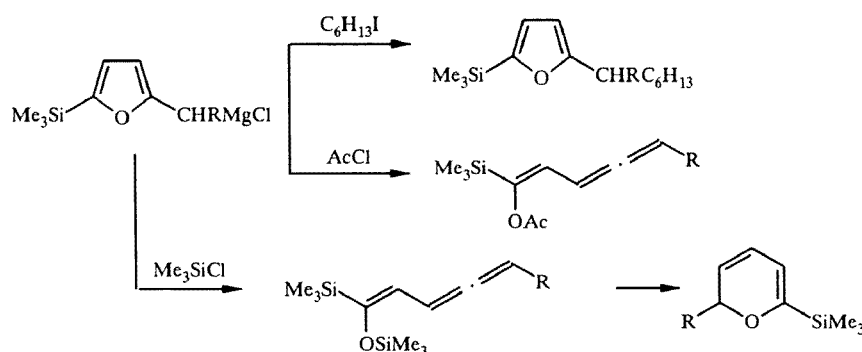


In the presence of copper iodide CuI a mixture of only two products (I) and (III) in a ratio of 79:21 is formed with an overall yield of 81%. Without the catalyst a mixture of all three products is obtained but with a preponderance of the product (II) (I:II:III = 16:77:7).

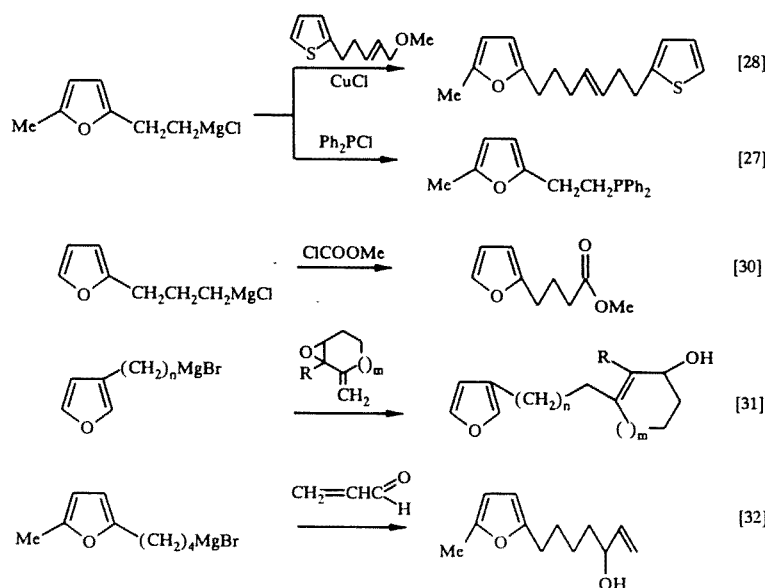
During the carbonylation of the benzofuran derivative with the CH_2MgCl substituent at position 3 only traces of (2-methyl-3-benzofuryl)acetic acid [33] and a small amount of 2,3-dimethylbenzofuran and 1,2-di(2-methyl-3-benzofuryl)ethane are formed. The main reaction product is 2-methyl-3-methylene-2,3-dihydro-2-benzofurancarboxylic acid.



The Grignard reagents obtained from 5-trimethylsilylfurfuryl chloride and its derivatives also exhibit anomalous properties in reactions with certain electrophiles. Whereas alkyl halides react at the furfuryl fragment in the presence of Li_2CuCl_4 , opening of the furan ring is observed under the influence of acyl chlorides and trimethylchlorosilane [26].



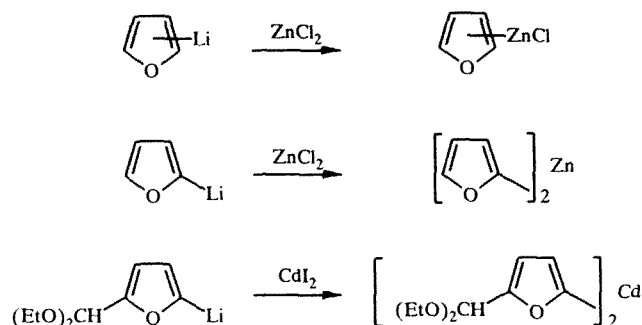
Some chemical transformations of furylethyl-, furylpropyl-, and furylbutylmagnesium halides were described [27-32].



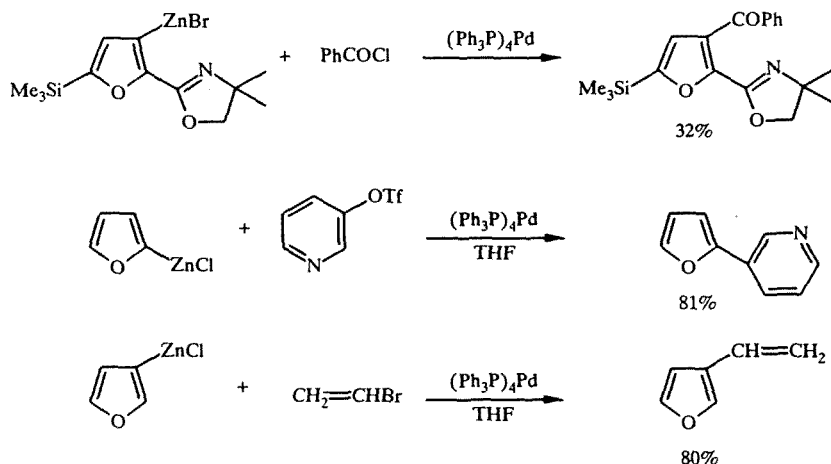
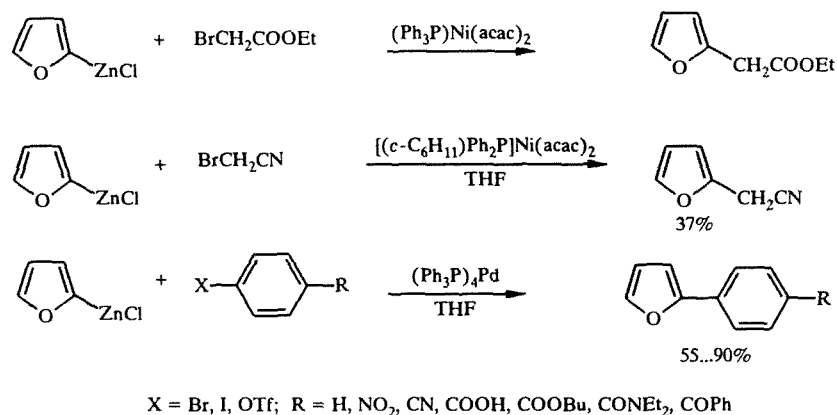
2. ORGANOZINC AND ORGANOCADMIUM DERIVATIVES

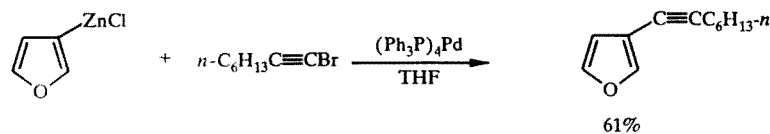
Among the furan derivatives of elements of the group II subgroup the zinc [51-60] and cadmium [61] compounds have been studied less. Mercury compounds on the other hand have been widely used in synthesis on account of the variety and simplicity of preparation and their adequate stability (including their stability in aqueous solutions).

The only method for the preparation of furan derivatives of zinc [51-58] and cadmium [59] with a $C_{\text{furan}}-\text{metal}$ bond is the reaction of the lithium derivatives of furan with zinc halides and cadmium iodide. As a rule, the reaction takes place at room temperature or with cooling to -20°C in THF or a mixture of THF and hexane.

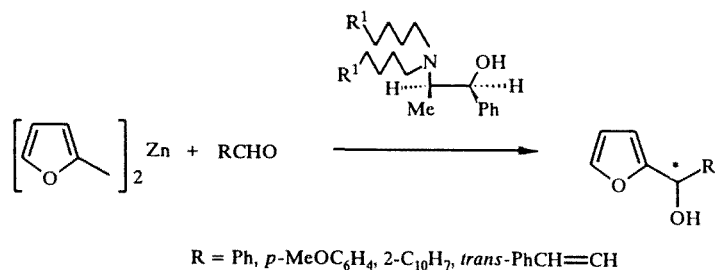


The 2- and 3-furyl derivatives of zinc react with various halogen derivatives [51-57, 59, 60] and triflates [58] at room temperature and when heated to 50°C in the presence of nickel and palladium catalysts $[(\text{Ph}_3\text{P})\text{Ni}(\text{acac})_2]$, $(\text{Ph}_3\text{P})_4\text{Pd}$, $(\text{AcO})_2\text{Pd}$, forming the cross-coupling products. This method was used for the synthesis of ethyl 2-furylacetate [54], 2-furylacetonitrile [57], furylbenzenes [51, 52, 56, 59, 60], polyheterocyclic systems [55], and vinyl- and ethynylfurans [52, 59].



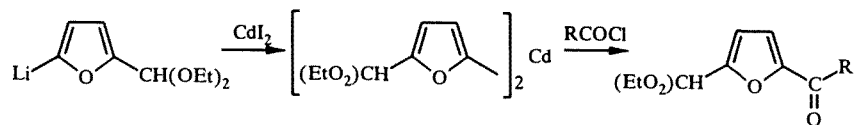


The enantioselective furylation of aldehydes was realized for the first time with di(2-furyl)zinc [53]. Optically active derivatives of furfuryl alcohol were obtained with high enantiomeric purity (up to 73%) by the enantioselective addition of difurylzinc to aldehydes in the presence of chiral catalysts: (1R,2S)-N,N-dibutylnorephedrine and (1R,2S)-N,N-di(4-phenylbutyl)norephedrine.



As a result of numerous experiments it was established [53] that lithium halides (lithium fluoride, chloride, bromide) increase the stereospecificity of the reaction. Thus, with the addition of difurylzinc to benzaldehyde in the presence of N,N-dibutylnorephedrine and lithium halides the optical yield of (S)-(2-furyl)phenylmethanol amounts to 53-56%. Without the lithium salts the yield is reduced to 11%. During comparison of the selectivity of the two employed catalysts preference can be given to (1S,2R)-N,N-di(4-phenylbutyl)norephedrine.

A compound of cadmium with a furyl group was obtained, as mentioned above, from a lithium derivative and was easily acylated by acid chlorides [61].



3. ORGANOMERCURY DERIVATIVES OF FURAN

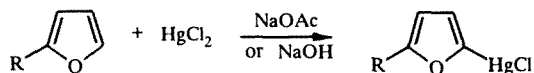
3.1. Synthesis

Three main methods have been used for the preparation of organomercury compounds of furan: The direct mercuration of furan and its derivatives; decarboxylation of the mercury salts of furancarboxylic acids; cyclization of unsaturated alcohols and glycols in the presence of mercury salts.

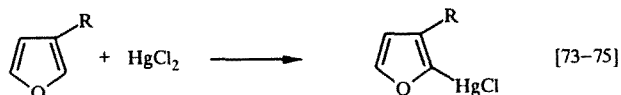
Various furans with the mercury atom at the α position of the ring were obtained by the action of mercury salts HgX_2 [$\text{X} = \text{Cl}, \text{AcO}, \text{C}(\text{NO}_2)_3, \text{OCN}$] on furan [62-65] and its 2- and 3-monosubstituted derivatives [66-74].



$\text{X} = \text{Cl}, \text{OAc}$ [62]; $\text{C}(\text{NO}_2)_3$ [63, 64]; OCN [65]

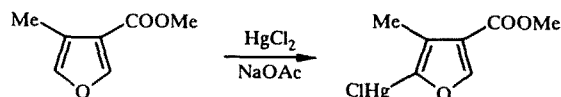


$\text{R} = \text{Alk}$ [66, 71, 72]; CH_2OH [67, 68]; CH_2OAc [69]; Cl [70]

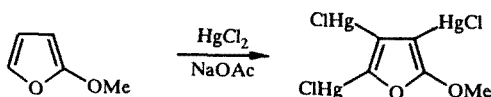


$\text{R} = \text{Me}, i\text{-Pr}$

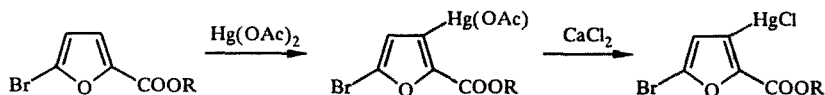
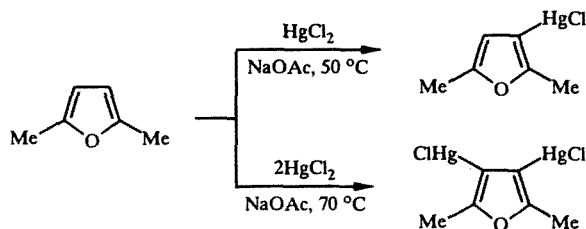
The monomercury chlorides and acetates of furan and its derivatives were obtained with yields of 35-70% in the reaction of equimolar amounts of mercuric chloride or acetate and the furan compound in the presence of sodium acetate in water or water-alcohol media. In the case of furan the 2,5-dimercuration product is also formed. The mercury salt of trinitromethane [63, 64] mercurates furan with a 25% yield, while mercury cyanate substitutes the hydrogen atom in the furan and sylvane under the influence of sodium acetate [65]. 3-Methyl-4-methoxycarbonylfuran is mercurated by mercuric chloride at position 2 of the furan ring [76].



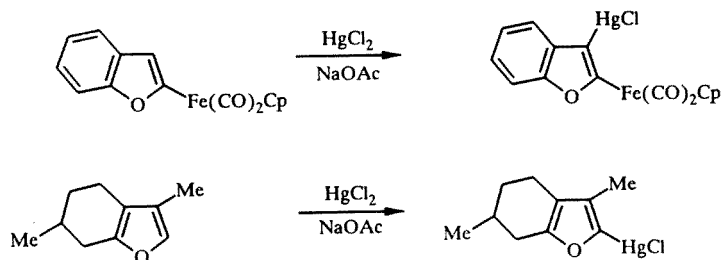
On the whole the α position of the furan ring is mercurated more readily than the β position. However, it is possible to mercurate the β position quite easily by the action of an excess of the mercurating agent [77] or by reaction with 2,5-disubstituted furans [78,79]. By the action of an excess of mercuric chloride on 2-methoxyfuran [77] it is possible to introduce the mercury substituents at all three free positions of the furan ring.



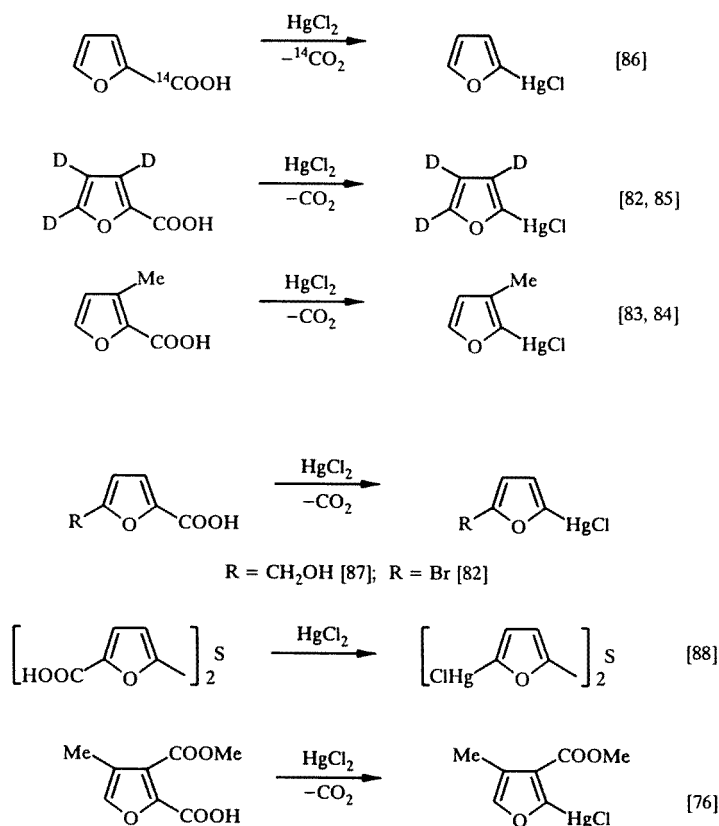
Depending on the ratio of the reagents, 2,5-dimethylfuran is mercurated by mercuric chloride to the mono- and dimercury derivative [78], while 5-bromo-2-furancarboxylic esters [79] are transformed into the corresponding 3-mercury-substituted compounds when treated with mercuric acetate.



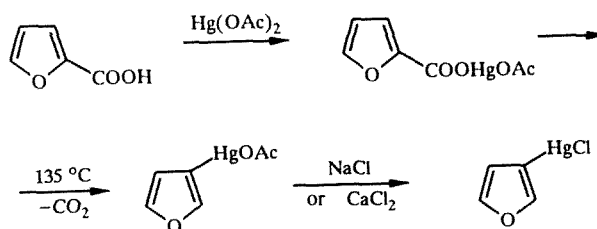
The σ -benzofuryl complex of cyclopentadienyldicarbonyliron reacts with mercuric chloride at the C–H bond at position 3 of the ring of the heterocyclic system [80], while 4,5,6,7-tetrahydro-3,6-dimethylbenzofuran reacts at the free position 2 of the ring [81].



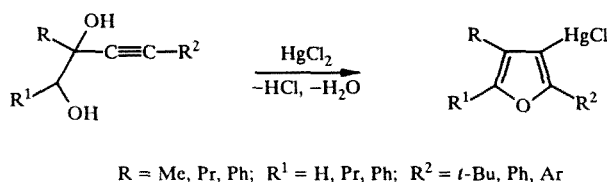
The second method for the synthesis of organomercury compounds involves decarboxylation of the mercury salts obtained in the reaction of furancarboxylic acids with mercuric chloride under alkaline conditions [62, 72, 82-88]. The furancarboxylic acid is usually treated with an aqueous solution of alkali and then with the mercury salt and heated until the release of carbon dioxide has stopped. It was established during investigation of this reaction that substitution of the carboxyl group by mercury takes place much more readily than direct substitution of the hydrogen atom.



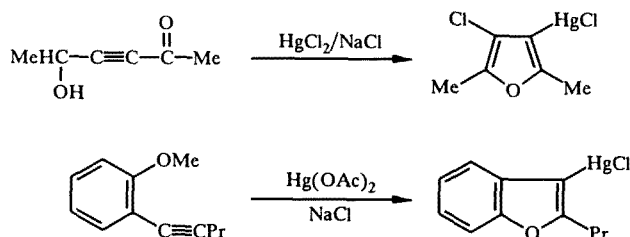
A mixed mercury salt is formed initially when 2-furancarboxylic acid is treated with mercuric acetate. When heated to 135°C it then undergoes rearrangement to 3-furylmercuric acetate [62, 89, 90].



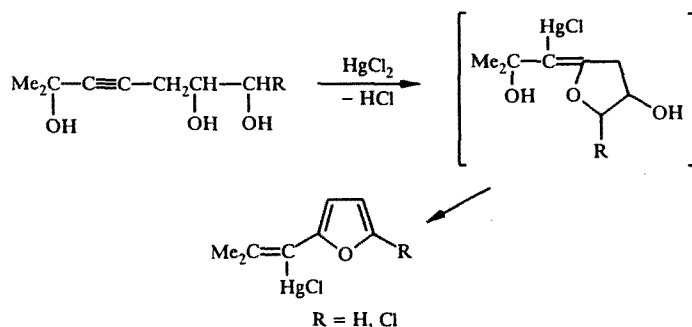
The cyclization of various derivatives of 3-butyne-1,2-diol with mercuric chloride at room temperature or with gentle heat has very often been used for the synthesis of organomercury compounds with the metal at position 3 of the furan ring [91-96]. The product yields amount to 40-50%.



2-Hydroxy-3-hexyn-5-one is converted by the action of mercuric chloride at 0°C in the dark into 2,5-dimethyl-3-mercuriofuran [97], while 1-(2-methoxyphenyl)-1-pentyne [98] is converted in the presence of mercuric acetate with subsequent treatment by sodium chloride into 2-propyl-3-chloromercuriobenzofuran. In all cases the mercury salt adds initially at the C≡C triple bond, and the following stage involves cyclization of the obtained compounds.

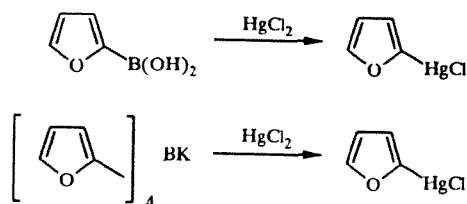


Furan derivatives in which the mercury atom is not directly attached to the heterocycle were synthesized with high yields (97-98%) by the intramolecular cyclization of acetylenic glycols [99].



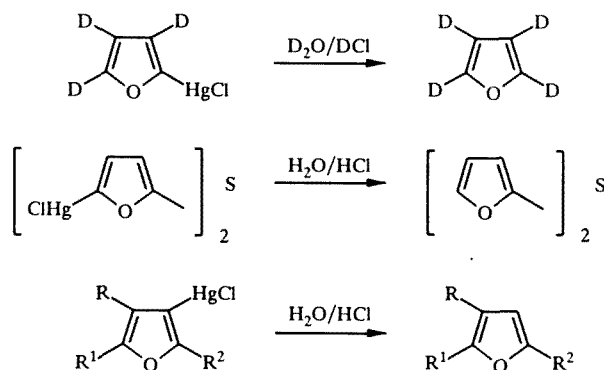
The cyclization of unsaturated alcohols has been used for the synthesis not only of furan derivatives but also of mercury derivatives of 2,5-dihydrofuran [100-107], tetrahydrofuran [108-120], and 2,3-dihydrobenzofuran [120-122].

Organomercury compounds are formed during cleavage of the C–B bond in 2-furylboronic acid [9] and tetra(2-furylboropotassium [123] with mercuric chloride. This is not, however, a preparative method and was only used to obtain evidence for the structure of the initial borofurans.

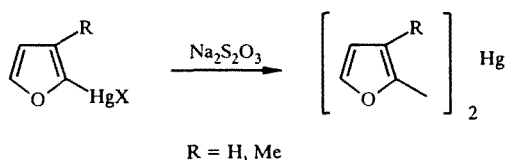


3.2. Chemical Properties

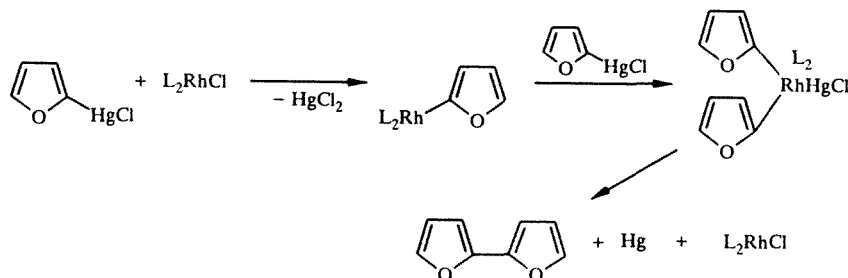
Compared with organolithium and organomagnesium compounds, the organomercury derivatives are less reactive. They are resistant to the action of water and alcohols, and many of the reactions are therefore conducted in water–alcohol media. Hydrolysis of the C–Hg bond can only be realized in strongly acidic media [82, 85, 88, 91-96, 124, 125].



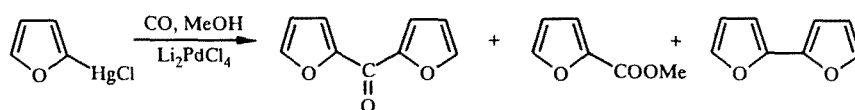
Furylmercuric chlorides can be easily converted into symmetrical derivatives of difurylmercury. The most suitable agent for this reaction is an aqueous solution of sodium thiosulfate [62, 83, 84, 126]. The yields of the symmetrical products amount to 60%.



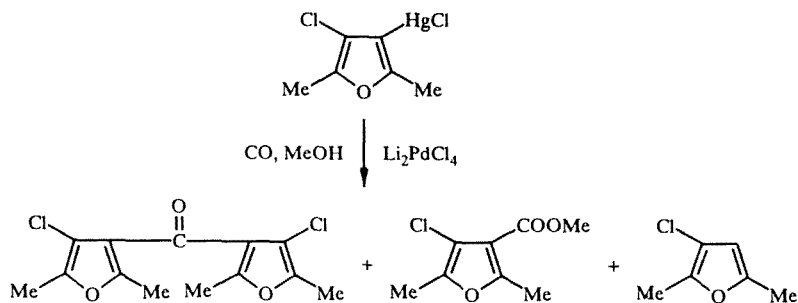
The action of the rhodium catalyst $[\text{ClRh}(\text{CO})_2]_2$ [127] on 2-furylmercuric chloride in hexamethylphosphorotriamide gives a 70% yield of 2,2'-bifuryl. In the opinion of the authors the role of the catalyst can be represented by the following scheme:



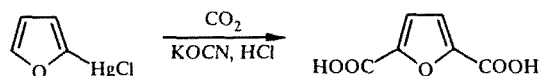
The catalytic carbonylation of 2-furylmercuric chloride was conducted in an autoclave at 100°C with carbon monoxide at a pressure of 50 atm. The salt Li_2PdCl_4 was used as catalyst. The main reaction products under these conditions are difuryl ketone and methyl 2-furancarboxylate. 2,2'-Bifuryl is also formed in small amounts [128].



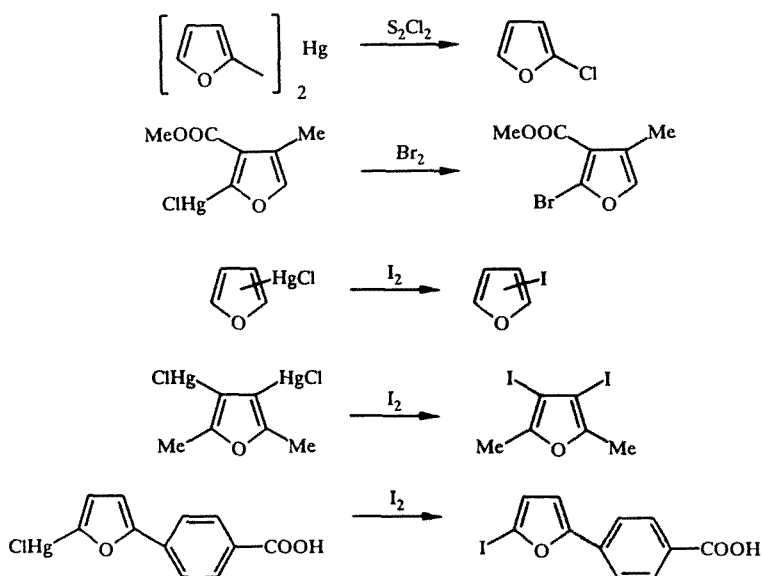
The carbonylation of 4-(2,5-dimethyl-3-chlorofuryl)mercuric chloride also takes place in a similar way [97]. The only difference is that the demercuration product is formed instead of the bifuryl compound.



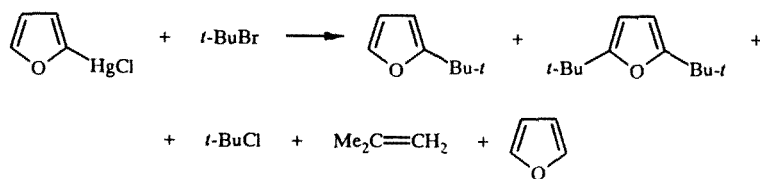
The reaction of carbon dioxide with 2-furylmercuric chloride at 200-350°C and 5-200 atm in the presence of KOCN followed by acidification with hydrochloric acid leads to 2,5-furandicarboxylic acid [129].



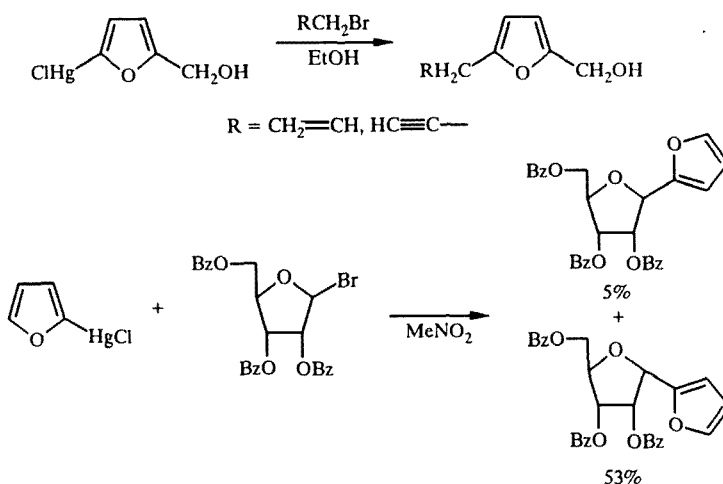
2-Chlorofuran can be obtained with a 60% yield from di(2-furyl)mercury by the action of freshly distilled disulfur dichloride S_2Cl_2 [126] in carbon disulfide, while the bromofuran [76] and iodofurans [62, 78, 98, 130] can be obtained by treatment of the furylmercuric chlorides with bromine and iodine respectively.



The reaction of mercury-substituted furans with bromoalkanes [66-68, 131-136] and also with iodoalkenes and iodoarenes [137-140] has been used most widely in the synthesis of furan compounds. When 2-furylmercury chloride is boiled with tert-butyl bromide for many hours in ethanol, alkylation at position 5 of the furan ring with the formation of di(tert-butyl)furan is observed in addition to substitution of the mercury group HgCl [66, 132]. However, recent investigations of this reaction by UV photoelectron spectroscopy [131] have shown that the reaction takes place in a more complicated manner with the formation of a mixture of 2-tert-butylfuran, 2,5-di(tert-butyl)furan, tert-butyl chloride, isobutylene, and furan.

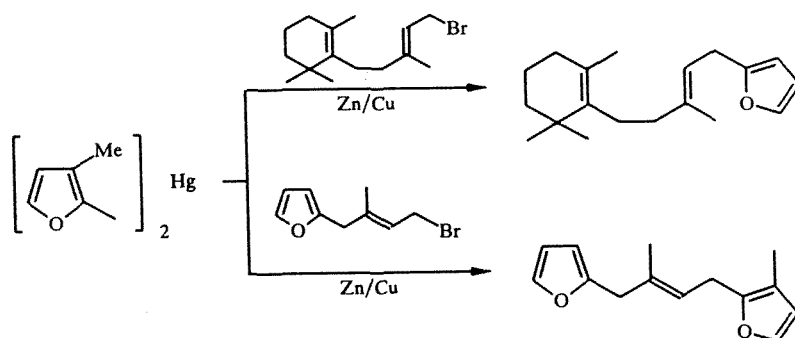


A series of bromine derivatives react with unsymmetrical mercury compounds without a catalyst when heated in chloroform [67, 68].

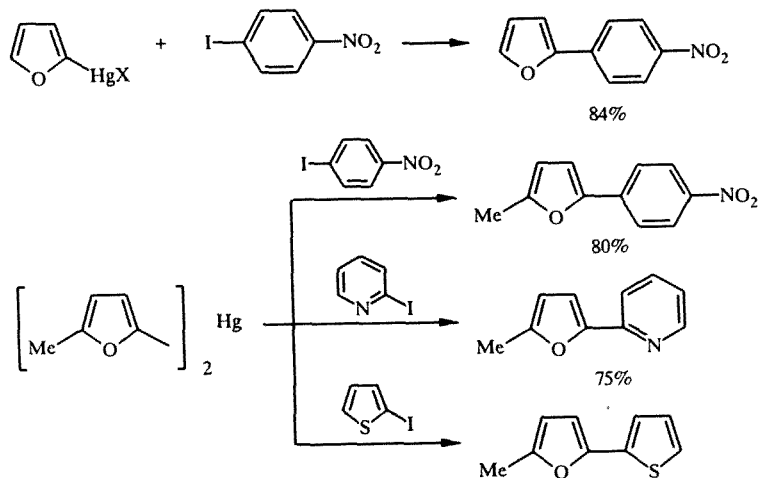


2,3,5-Tri-O-benzoyl-D-ribofuranosyl bromide in nitromethane at room temperature forms a mixture of anomers with 2-furylmercuric chloride with an overall yield of 58% [133].

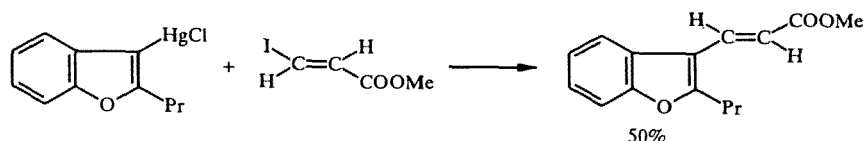
Zinc-copper dust as catalyst is essential for the symmetrical mercury derivatives in reactions with bromoalkanes [134-136].



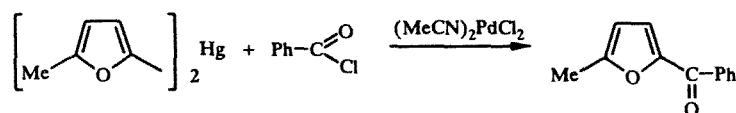
Iodoarenes [137-139] and iodoalkenes [140] only react with symmetrical and unsymmetrical mercury derivatives of furan in the presence of palladium [137-139] and rhodium [140] catalysts. Arylation of the furan ring by a coupling reaction is a convenient method for the production of arylfurans. The reaction takes place under the influence of $(\text{Ph}_3\text{P})_2\text{PdIPh}$, $(\text{Ph}_3\text{P})_2\text{PdCl}_2$, $(\text{MeCN})_2\text{PdCl}_2$, PdCl_2 , and iodine ions (Bu_4NI in HMPTA and NaI in acetone) at room temperature and gives high yields.



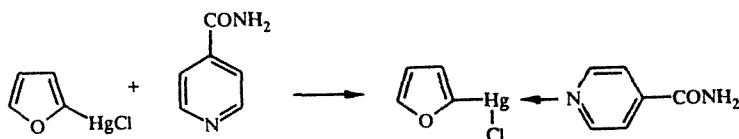
In the presence of lithium chloride in hexamethylphosphorotriamide the rhodium catalyst $(\text{Ph}_3\text{P})_3\text{RhCl}$ catalyzes the alkenylation of the mercury derivative of benzofuran [140].



Furylmercuric chlorides are inactive in reactions with acid chlorides. For example, the 2-furyl derivative of mercury does not react with benzoyl or furanecarbonyl chlorides and only forms methyl-2-furyl ketone with acetyl chloride with a yield of 21% [62]. With the palladium catalyst $(\text{MeCN})_2\text{PdCl}_2$ it was possible to couple di(5-methyl-2-furyl)mercury with benzoyl chloride and to obtain a 92% yield of phenyl 5-methyl-2-furyl ketone [141, 142].

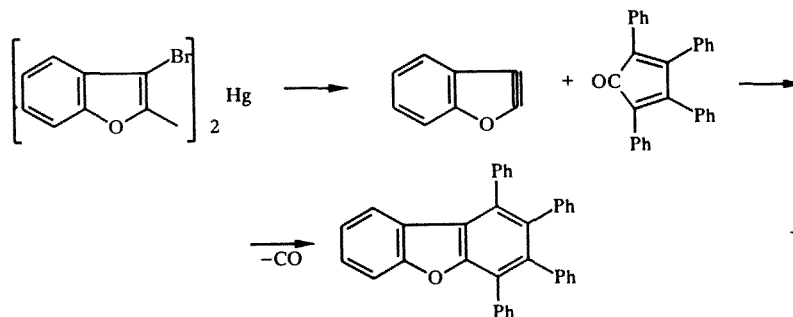


The formation of a complex of 2-furylmercuric chloride with isonicotinamide was investigated. The reaction takes place in THF at room temperature in 2 h [143].

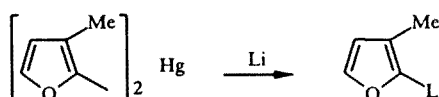


Di(2-furyl)mercury forms complexes $(2\text{-furyl})_2\text{Hg}\cdot\text{L}$ with 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline, and 3,4,7,8-tetramethyl-1,10-phenanthroline in ethanol [144].

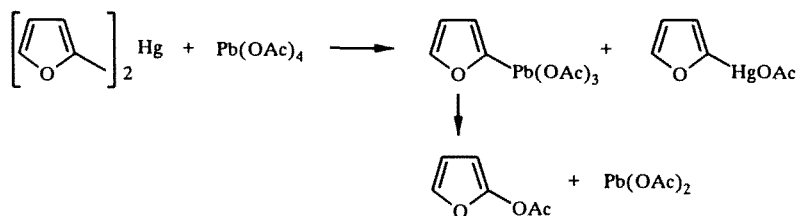
The possibility of the formation of the unstable intermediate product 2,3-dehydrobenzofuran from a mercury derivative was mentioned in [145]. This product enters into diene synthesis with 1,2,3,4-tetraphenyl-1,3-cyclopentadien-5-one.



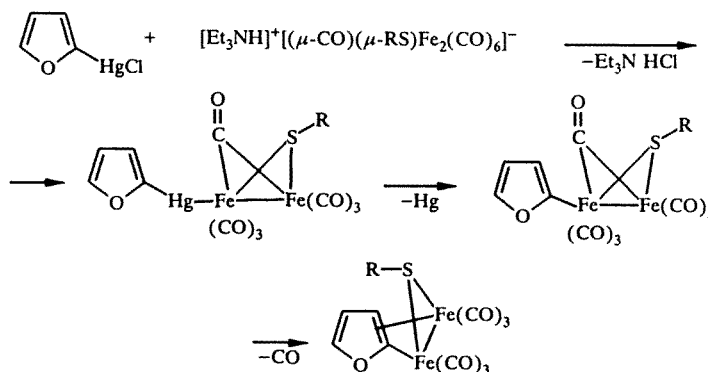
The possibilities of using the organomercury derivatives of furan for the production of organometallic compounds were studied. With a suspension of lithium in ether at -20°C di(3-methyl-2-furyl)mercury gives the corresponding lithium derivative [83, 84].



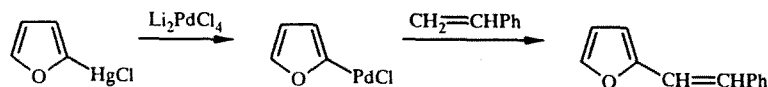
2-Furylmercury chloride does not react with tetrachlorosilane, triethylchlorosilane [146], and triphenylchlorostannane [147], but in reaction with triethylsilane furylmercury chloride is reduced, and mercury is released [146]. With di(2-furyl)mercury lead tetraacetate forms an unstable furyl derivative of lead, which quickly decomposes with the formation of 2-acetoxymethylfuran [148].



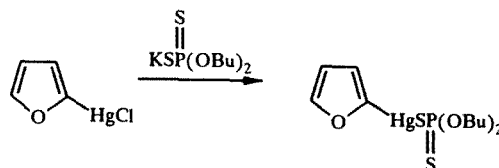
The furan derivatives of mercury were used for the production of iron [149] and palladium [150] compounds. Di(2-furyl)mercury and 2-furylmercuric chloride react with iron complexes $[\text{Et}_3\text{NH}]^+[(\mu\text{-CO})(\mu\text{-RS})\text{Fe}_2(\text{CO})_6]^-$ with the formation of a binuclear complex, in which according to x-ray crystallographic analysis one iron atom is σ -bonded to the carbon atom of furan ring at position 2, while the second is π -bonded with the $\text{C}=\text{C}$ double bond [149]. The proposed reaction mechanism is presented in the scheme:



2-Furypalladium chloride [150], produced *in situ* from 2-furylmercuric chloride and lithium tetrachloropalladate, then reacts with olefins with the formation of furylalkenes and 2,2'-bifuryl as impurity.



In furylmercuric acetates the acetate group can be substituted easily and quantitatively by chlorine by the action of an excess of sodium or potassium chloride [62, 89, 98, 114], while the chlorine in 2-furylmercuric chloride is substituted by the dibutylthiophosphate group [151] during treatment with potassium dibutyl dithiophosphate.



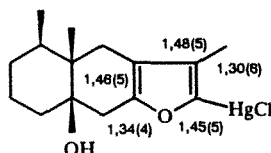
3.3. Physicochemical Characteristics

The physicochemical investigations of the furan derivatives of mercury are few and concern the following processes: Polarographic reduction of symmetrical organomercury compounds R_2Hg of the α - and β -substituted furan series [152]; UV photoelectron spectroscopy of R_2Hg and RHgX compounds [153]; comparison of the experimental and calculated frequencies in the IR spectra of 2- and 3-furylmercuric chlorides [154]; NMR spectroscopy of the mercury compounds of furan [155-158]; x-ray crystallographic analysis of a furyl derivative of mercury [159].

Polarographic reduction of the C–Hg bond in anhydrous dimethylformamide takes place more readily for all the 2-furyl derivatives than for the analogous 3-substituted derivatives. This follows from the lower values of the half-wave potential ($E_{1/2}$) in compounds of the first type [152]. According to the data from photoelectron spectroscopy [153], weak interaction is observed between the π orbitals of the ring and the unoccupied $6p\pi$ orbitals of the mercury in di(2-furyl)mercury. However, this interaction is somewhat greater than for di(3-furyl)mercury. The HgCl group has a weak electron-withdrawing effect in relation to the ring.

The NMR spectra of di(2-furyl)mercury were studied. ^1H NMR spectrum (δ , ppm): H(2), 6.66; H(3), 6.75; H(4), 8.01 [155]. ^{13}C NMR spectrum: C(2), 189.5; C(3), 121.2; C(4), 109.6; C(5), 146.7 [156]. The proton spin–spin coupling constants for this compound [155] and 3-furylmercuric chloride [158] differ little from the furan constants. A linear correlation is observed between the $^{119}\text{Hg}-^1\text{H}$ and $^1\text{H}-^1\text{H}$ spin–spin coupling constants [155, 157], indicating that Fermi contact makes a major contribution to the transmission of the spin coupling [157].

In order to establish the structure of one of the toxic compounds isolated from *Tetradymia glabrata* an x-ray crystallographic analysis of its mercury derivative was undertaken [159].



The furan ring is almost coplanar. The mean deviation of the five ring atoms amounts to 0.03 Å, while the maximum deviation (0.05 Å) is observed for the C(2) carbon atom attached to the mercury atom. The C–Hg–Cl fragment in the molecule is almost linear (CHgCl bond angle 174°). The lengths of the Hg–C and Hg–Cl bonds are 2.03(2) and 2.30(1) Å.

3.4. Biological Activity

The *in vitro* fungicidal activity of 3-chloromercuriofurfural was investigated on the following types of fungi: *Trichophyton purpureum*, *T. interdigitale*, *T. asteroides*, and *Candida albicans*. The minimum concentration of the compound that inhibits the growth of the fungi is 6.25, 12.5, 6.25, and 25.0 $\mu\text{g/ml}$ respectively [160]. 5-Chloromercuriofurfural and 5-chloromercuriofurfuryl alcohol act *in vitro* on ascarides in pigs [161].

Di(2-furylethynyl)mercury exhibits high fungistatic activity. Thus, the minimum concentration for the inhibition of *T. asteroides*, *Piricularia oryzae*, and *C. albicans* amounts to 0.2-0.8 $\mu\text{g/ml}$; the bacteriostatic activity of this compound is also fairly high toward Gram-negative (*Escherichia coli*, 1.6 $\mu\text{g/ml}$) and Gram-positive (*Bacillus subtilis*, 1.6 $\mu\text{g/ml}$) bacteria. Unsymmetrical 2-furylethynylmercuric chloride exhibits a significantly smaller fungistatic effect (50 $\mu\text{g/ml}$) [162]. At the same time the antimicrobial activity against phytophthorosis in potatoes and powdery mildew in barley is higher for 2-furylethynylmercuric chloride *in vitro* and *in vivo* than for the symmetrical mercury derivative [163].

Di(2-furylethynyl)mercury suppresses the growth of the spores of the pathogenic microorganisms *Cochliobolus miyabeanus* [164]. However, the effect of the furyl derivative is somewhat lower than the effect of the benzyl and phenyl analogs.

The phytotoxicity of the investigated ethynyl derivatives of mercury was investigated in relation to rice, rye, cucumbers, radish, peaches, pears, and grapes. Cucumbers proved resistant to their action, while peaches, pears, and radishes were extremely sensitive [165]. The phytotoxicity of 2-furylethynylmercuric chloride was higher than that of di(2-furylethynyl)mercury.

REFERENCES

1. É. Lukevits and O. A. Pudova, Khim. Geterotsikl. Soedin., No. 4, 435 (1995).
2. A. F. Shepard, N. R. Winslow, and J. R. Johnson, J. Am. Chem. Soc., **52**, 2083 (1930).
3. C. F. H. Allen and H. B. Rosener, J. Am. Chem. Soc., **49**, 2110 (1927).
4. B. A. Tertov, Z. N. Nazarova, Yu. A. Gabaraeva, and N. V. Shibaeva, Zh. Org. Khim., **8**, 1081 (1972).
5. H. E. Ramsden, US Patent No. 2,959,589, Chem. Abs., **55**, 5548b (1961).
6. H. Normant, Bull. Soc. Chim. Fr., No. 5, 728 (1957).
7. A. Takeda, K. Shinhamma, and S. Tsuboi, Bull. Chem. Soc. Jpn., **50**, 1903 (1977).
8. A. Takeda, K. Shinhamma, and S. Tsuboi, J. Org. Chem., **45**, 3125 (1980).
9. J. R. Johnson, M. G. Van Campen, and O. Grummitt, J. Am. Chem. Soc., **60**, 111 (1938).
10. G. J. Martin, B. Mechin, Y. Leroux, C. Paulmier, and J. C. Meunier, J. Organomet. Chem., **67**, 327 (1974).
11. E. Sherman and E. D. Amstutz, J. Am. Chem. Soc., **72**, 2195 (1950).
12. S. P. Tanis, Tetrahedron Lett., **23**, 3115 (1982).
13. S. P. Tanis, Y. H. Chuang, and D. B. Head, J. Org. Chem., **53**, 4929 (1988).
14. O. S. Park and W. Y. Lee, Yakhak Hoechi, **31**, 10 (1987); Chem. Abs., **108**, 112767 (1988).
15. M. Kato, M. Watanabe, B. Vogler, Y. Tooyama, and A. Yoshikoshi, J. Chem. Soc., Chem. Commun., No. 23, 1706 (1990).
16. S. P. Tanis and D. B. Head, Tetrahedron Lett., **25**, 4451 (1984).
17. S. P. Tanis and D. B. Head, Tetrahedron Lett., **23**, 5509 (1982).
18. S. P. Tanis, Y. H. Chuang, and D. B. Head, Tetrahedron Lett., **26**, 6147 (1985).
19. A. Carpita, F. Bonaccorsi, and R. Rossi, Gazz. Chim. Ital., **114**, 443 (1984).
20. S. P. Tanis and P. M. Herrinton, J. Org. Chem., **48**, 4572 (1983).
21. S. C. Welch, A. S. C. P. Rao, J. T. Lyon, and G. M. Assercq, J. Am. Chem. Soc., **105**, 252 (1983).
22. S. Araki and Y. Butsugan, Chem. Lett., No. 2, 177 (1982).
23. S. Araki and Y. Butsugan, Bull. Chem. Soc. Jpn., **56**, 1446 (1983).
24. J. Bosch, M. Alvarez, R. Llobera, and M. Feliz, An. Quim., **75**, 712 (1979).
25. R. Grandos Jarque, J. Bosch Cartes, R. Llobera Jimenez, C. Martinez Roldan, and F. Rabadan Peinado, Spanish Patent No. 467,249, Chem. Abs., **92**, 6427 (1980).
26. K. Takanishi, H. Urabe, and I. Kuwajima, Tetrahedron Lett., **28**, 2281 (1987).

27. E. Lindner and C. Scheytt, *Z. Naturforsch. B*, **41**, 10 (1986).
28. A. Corvers, P. C. H. Scheers, J. W. Denaan, and H. M. Buck, *Rec. Trav. Chim.*, **96**, 279 (1977).
29. A. Corvers, J. H. Vanmil, M. M. E. Sap, and H. M. Buck, *Rec. Trav. Chim.*, **96**, 18 (1977).
30. B. P. Gunn, *Tetrahedron Lett.*, **26**, 2869 (1985).
31. S. P. Tanis, P. M. Herrinton, and L. A. Dixon, *Tetrahedron Lett.*, **26**, 5347 (1985).
32. S. J. Burrell, A. E. Derome, M. S. Edenborough, L. M. Harwood, S. A. Leeming, and N. S. Isaacs, *Tetrahedron Lett.*, **26**, 2229 (1985).
33. R. Gaertner, *J. Am. Chem. Soc.*, **74**, 5319 (1952).
34. N. I. Shuikin and G. K. Vasilevskaya, *Dokl. Akad. Nauk SSSR*, **159**, 395 (1964).
35. R. Onesta and A. Ferretti, *Gazz. Chim. Ital.*, **85**, 288 (1955).
36. R. Onesta, A. Ferretti, and B. Notari, *Gazz. Chim. Ital.*, **86**, 178 (1956).
37. C. F. Ingham, R. A. Massy-Westropp, and G. D. Reynolds, *Aust. J. Chem.*, **27**, 1477 (1974).
38. A. Holy and A. Vystřil, *Coll. Czech. Chem. Commun.*, **27**, 1861 (1962).
39. B. M. Trost, M. Lautens, M. H. Hung, and C. S. Carmichael, *J. Am. Chem. Soc.*, **106**, 7641 (1984).
40. R. Sjöholm, *Acta Chem. Scand. B*, **31**, 278 (1977).
41. B. Gustafsson, *Acta Chem. Scand. B*, **31**, 382 (1977).
42. G. A. Holmberg, M. Wennström, and M. Grönland, *Acta Chem. Scand. B.*, **29**, 728 (1975).
43. I. I. Lapkin, N. V. Bogoslovskii, and F. G. Saitkulova, *Zh. Org. Khim.*, **2**, 156 (1966).
44. Yu. P. Dormidontov and L. P. Shadrina, *Zh. Org. Khim.*, **19**, 269 (1983).
45. S. Benetti, R. Chiron, and Y. Graff, *C.r.C.*, **283**, 351 (1976).
46. S. Vikhert, *Zh. Org. Khim.*, **18**, 2223 (1982).
47. I. S. Berdinskii, L. V. Kazakova, G. P. Petyunin, P. A. Petyunin, and V. P. Baboshko, *Zh. Org. Khim.*, **10**, 2077 (1974).
48. R. Gauthier, G. P. Axiotis, and M. Chastrette, *J. Organomet. Chem.*, **140**, 245 (1977).
49. Sh. Mamedov, M. A. Avanesyan, B. M. Alieva, *Zh. Obshch. Khim.*, **34**, 478 (1964).
50. R. E. Lutz and J. M. Smith, Jr., *J. Am. Chem. Soc.*, **63**, 1148 (1941).
51. C. Amatore, A. Jutand, S. Negri, and J. F. Fauvarque, *J. Organomet. Chem.*, **390**, 389 (1990).
52. E. Negishi, F. T. Luo, R. Frisbee, and H. Matsushita, *Heterocycles*, **18**, 117 (1982).
53. K. Soai and Y. Kawase, *J. Chem. Soc. Perkin I*, No. 11, 3214 (1990).
54. T. Klingstedt and T. Frejd, *Organometallics*, **2**, 598 (1983).
55. A. Minato, K. Suzuki, K. Tamao, and M. Kumada, *J. Chem. Soc., Chem. Commun.*, No. 8, 511 (1984).
56. A. Pelter, M. Rowlands, and I. H. Jenkins, *Tetrahedron Lett.*, **28**, 5213 (1987).
57. T. Frejd and T. Klingstedt, *Synthesis*, No. 1, 40 (1987).
58. A. Arcadi, A. Burini, S. Cacchi, M. Delmastro, F. Marinelli, and B. Pietroni, *Synlett.*, No. 1, 47 (1990).
59. D. S. Ennis and T. L. Gilchrist, *Tetrahedron*, **46**, 2623 (1990).
60. F. T. Luo and R. T. Wang, *Heterocycles*, **32**, 2623 (1990).
61. B. A. Tertov, Z. N. Nazarova, Yu. A. Gabaraeva, and N. V. Shibaeva, *Zh. Obshch. Khim.*, **7**, 1062 (1971).
62. A. P. Dunlop and F. N. Peters, *The Furans*, Reinhold Publishing Corporation, New York, Ch. 6, 193 (1953).
63. S. S. Novikov, T. I. Godovikova, and V. A. Tartakovskii, *Izv. Akad. Nauk SSSR. Ser. Khim.*, No. 3, 505 (1960).
64. S. S. Novikov, T. I. Godovikova, and V. A. Tartakovskii, *Izv. Akad. Nauk SSSR. Ser. Khim.*, No. 3, 505 (1960).
65. E. Söderbäck, *Acta Chem. Scand. B.*, **13**, 1221 (1959).
66. W. H. Brown and G. F. Wright, *Can. J. Chem.*, **35**, 236 (1957).
67. S. Katsuda, Japanese Patent No. 6,927,230, *Chem. Abs.*, **72**, 43420 (1970).
68. S. Katsuda, Japanese Patent No. 7,123,729, *Chem. Abs.*, **75**, 98429 (1971).
69. T. Okuzumi, *Nippon Kagaku Zasshi*, **79**, 1371 (1958).
70. R. Dowbenko, *Chem. Ind.*, **32**, 1425 (1965).
71. C. A. Giller, A. A. Anderson, A. É. Berzinya, and M. V. Shimanskaya, *Izv. Akad. Nauk SSSR. Ser. Khim.*, No. 5, 575 (1965).
72. M. Fetizon and P. Baranger, *Compt. Rend.*, **234**, 2296 (1952).
73. J. P. Katney, H. W. Henssen, and N. G. Vijayakumaran, *Tetrahedron*, **27**, 3323 (1971).
74. H. Gilman and R. Burtner, *J. Am. Chem. Soc.*, **55**, 859 (1933).

75. H. Gilman and R. Burtner, *J. Am. Chem. Soc.*, **55**, 2903 (1933).
76. H. Gilman and R. Burtner, *J. Am. Chem. Soc.*, **71**, 1213 (1949).
77. G. M. Donald and E. D. Amstutz, *J. Org. Chem.*, **21**, 516 (1956).
78. C. D. Hurd and K. Wilkinson, *J. Am. Chem. Soc.*, **70**, 739 (1948).
79. W. W. Beck and C. S. Hamilton, *J. Am. Chem. Soc.*, **60**, 620 (1938).
80. A. N. Nesmeyanov, N. E. Kolobova, L. V. Goncharenko, and K. N. Anisimov, *Izv. Akad. Nauk SSSR. Ser. Khim.*, No. 5, 1179 (1976).
81. R. H. Eastman, *J. Am. Chem. Soc.*, **72**, 5313 (1950).
82. D. J. Chadwick, J. Chambers, P. K. G. Hodgson, G. C. Meakins, and R. L. Snowden, *J. Chem. Soc. Perkin I*, **10**, 1141 (1974).
83. G. Büchi, E. Kovats, P. Enggist, and G. Uhde, *J. Org. Chem.*, **33**, 1227 (1968).
84. Y. Gopichand, R. S. Prasad, and K. K. Chakravarti, *Tetrahedron Lett.*, No. 52, 5177 (1973).
85. D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J. Chem. Soc., Perkin I*, No. 3, 201 (1973).
86. W. A. Bonner and M. R. Roth, *J. Am. Chem. Soc.*, **81**, 5454 (1959).
87. C. D. Cottet and M. S. Feather, *Carbohydr. Res.*, **98**, 173 (1981).
88. Z. E. Nazarova and Yu. A. Babaev, *Zh. Obshch. Khim.*, **34**, 4010 (1964).
89. J. T. Wrobel and Z. Dabrowski, *Rocz. Chem.*, **40**, 503 (1966).
90. S. Gronowitz and G. Sörlin, *Arkiv Kemi*, **19**, 515 (1963).
91. A. Fabritsy and É. D. Venus-Danilova, *Zh. Obshch. Khim.*, **28**, 3227 (1958).
92. A. Fabritsy and S. Goshchinskii, *Zh. Obshch. Khim.*, **29**, 81 (1959).
93. A. Fabritsy and I. Kubalya, *Zh. Obshch. Khim.*, **30**, 3604 (1960).
94. A. Fabritsy and I. Kubalya, *Zh. Obshch. Khim.*, **31**, 476 (1961).
95. A. Fabrycy and Z. Wichert, *Rocz. Chem.*, **42**, 35 (1968).
96. A. Fabrycy and Z. Wichert, *Rocz. Chem.*, **51**, 249 (1977).
97. R. C. Larock and C. L. Liu, *J. Org. Chem.*, **48**, 2151 (1983).
98. R. C. Larock and L. W. Hareison, *J. Am. Chem. Soc.*, **106**, 4218 (1984).
99. N. N. Baranov, M. S. Malinovskii, and M. P. Khmel', *Khim. Geterotsikl. Soedin.*, No. 9, 1164 (1977).
100. F. Toda and K. Akagi, *Tetrahedron*, **25**, 3795 (1969).
101. F. Toda, N. Odi, and K. Akagi, *Bull. Chem. Soc. Japan*, **44**, 1050 (1971).
102. A. J. Bridges, R. D. Thomas, *J. Chem. Soc., Chem. Commun.*, No. 11, 694 (1984).
103. É. D. Venus-Danilova and A. Fabritsy, *Zh. Obshch. Khim.*, **26**, 2458 (1956).
104. É. D. Venus-Danilova and A. Fabritsy, *Zh. Obshch. Khim.*, **26**, 1901 (1956).
105. A. Fabritsy [Fabrycy] and P. Dobrzenetskaya (Dobrzeńska), *Zh. Obshch. Khim.*, **37**, 60 (1967).
106. A. Fabrycy and R. Dobrzeńska, *Rocz. Chem.*, **41**, 1733 (1967).
107. G. B. Gill and M. S. H. Idris, *Tetrahedron Lett.*, **26**, 4811 (1985).
108. H. B. Henbest and B. Nichols, *J. Chem. Soc.*, 277 (1959).
109. B. Giese, K. Henck, H. Lenhardt, and U. Leining, *Chem. Ber.*, **117**, 2132 (1984).
110. J. Barluenga, J. Lopezpradu, P. J. Campos, and G. Asensio, *Tetrahedron*, **39**, 2863 (1983).
111. M. C. Benhamou, G. Etemad-Moghadam, V. Speziale, and A. Lattes, *J. Heterocycl. Chem.*, **15**, 1313 (1978).
112. R. Amouroux, F. Chastrette, and M. Chastrette, *J. Heterocycl. Chem.*, **18**, 565 (1981).
113. S. S. Novikov, V. A. Tartakovskii, T. I. Godovikova, and V. G. Gribov, *Izd. Akad. Nauk SSSR. Ser. Khim.*, No. 2, 272 (1962).
114. R. L. Rowland, *J. Am. Chem. Soc.*, **73**, 2381 (1951).
115. V. Speziale, J. Roussel, and A. Lattes, *J. Heterocycl. Chem.*, **11**, 771 (1974).
116. A. V. Gomez, M. J. Barluenga, M. Yus Asfiz, *Rev. Acad. Cienc. Exactas. Fís.-Quím. Natur. Zaragoza*, **28**, 225 (1973).
117. V. Speziale and A. Lattes, *J. Heterocycl. Chem.*, **16**, 465 (1979).
118. R. Ya. Levina, T. I. Tantsyreva, V. N. Vinogradova, and E. G. Treshchova, *Dokl. Akad. Nauk SSSR*, **85**, 107 (1952).
119. R. L. Rowland, W. L. Perry, and H. L. Friedman, *J. Am. Chem. Soc.*, **73**, 1040 (1951).
120. E. A. Shilov and I. M. Vasil'kevich, *Ukr. Khim. Zh.*, **33**, 1044 (1967).

121. A. S. Fomenko, G. P. Miklukhin, and E. A. Sadovnikova, *Dokl. Akad. Nauk SSSR*, **62**, 91 (1948).
122. A. S. Fomenko and E. A. Sadovnikova, *Zh. Obshch. Khim.*, **20**, 1898 (1950).
123. A. N. Nesmeyanov, V. A. Sazonova, and V. N. Drozd, *Izv. Akad. Nauk SSSR. Ser. Khim.*, No. 1, 163 (1959).
124. D. J. Chadwick, J. Chambers, G. D. Meakins, and R. L. Snowden, *J. Chem. Soc. Chem. Commun.*, No. 12, 742 (1972).
125. S. Saltzer, *Tetrahedron Lett.*, 457 (1962).
126. M. N. M. Khodeir, L. Skulski, and P. Wroczynski, *Bull. Pol. Acad. Sci. Chem.*, **34**, 443 (1986).
127. R. C. Larock and J. C. Bernhardt, *J. Org. Chem.*, **42**, 1680 (1977).
128. Y. Izumi, T. Iino, and A. Kasahara, *Bull. Chem. Soc. Jpn.*, **46**, 2251 (1973).
129. H. Schütt, German Patent No. 1,096,367, *Chem. Abs.*, **55**, 25984a (1961).
130. L. Fisera, J. Sura, J. Kovac, and M. Lucky, *Coll. Czech. Chem. Commun.*, No. 39, 1711 (1974).
131. L. Nyulaszi, A. Gyuricza, and T. Veszpremi, *Tetrahedron*, No. 43, 5955 (1987).
132. D. J. Milner, British Patent No. 2,084,995, *Chem. Abs.*, **97**, 72242 (1982).
133. I. Maeba, K. Iwata, F. Usami, and H. Furukawa, *J. Org. Chem.*, **48**, 2998 (1983).
134. T. Kato, M. Tanemura, S. Kauno, T. Suzuki, and Y. Kitahara, *Bioorg. Chem.*, **1**, 84 (1971).
135. N. Fukamiya and S. Yasuda, *Chem. Ind.*, No. 4, 126 (1979).
136. T. Kato, M. Tanemura, and Y. Kitahara, Japanese Patent No. 7,210,388, *Chem. Abs.*, **77**, 75356 (1972).
137. N. A. Bumagin, I. O. Kalinovskii, and I. P. Beletskaya, *Khim. Geterotsikl. Soedin.*, No. 11, 1467 (1983).
138. I. P. Beletskaya, *J. Organomet. Chem.*, **250**, 551 (1983).
139. N. A. Bumagin, P. G. More, and I. P. Beletskaya, *J. Organomet. Chem.*, **364**, 231 (1989).
140. R. C. Larock, K. Narayanan, and S. S. Hersherberger, *J. Org. Chem.*, **48**, 4377 (1983).
141. N. A. Bumagin, P. G. More, and I. P. Beletskaya, *J. Organomet. Chem.*, **365**, 379 (1989).
142. N. A. Bumagin, P. G. More, and I. P. Beletskaya, *Metalloorgan. Khim.*, **2**, 351 (1989).
143. S. Bhatia, N. K. Kaushik, and G. S. Sodhi, *Z. Naturforsch. B*, **34**, 318 (1988).
144. N. A. Bell and R. M. King, *J. Organomet. Chem.*, **179**, 133 (1979).
145. G. Wittig, *Rev. Chim. Acad. Rep. Populaire Roumaine*, **7**, 1393 (1962).
146. É. Lukevits and S. Giller, *Izv. Akad. Nauk Latv. SSR. Khim.*, No. 4, 99 (1961).
147. H. Gillman and T. N. Goreau, *J. Org. Chem.*, **17**, 1470 (1952).
148. J. T. Pinhey and E. G. Roche, *J. Chem. Soc. Perkin I*, No. 8, 2415 (1988).
149. D. Seyferth, L. L. Anderson, F. Villafane, M. Cowie, and R. W. Hilt, *Organometallics*, **11**, 3262 (1992).
150. A. Kasahara, T. Izumi, G. Saito, and T. Takeda, *Asahi Garasu Kogyo Gijutsu Shoreikai Kenkyu Hokoku*, **22**, 95 (1973). *Chem. Abs.*, **81**, 135859 (1974).
151. M. Nagasawa, T. Maeda, and T. Sato, Japanese Patent No. 17,570, *Chem. Abs.*, **59**, 11559 (1963).
152. K. P. Butin, L. G. Yudin, A. I. Pavlyuchenko, I. P. Beletskaya, and A. N. Kost, *Zh. Org. Khim.*, **7**, 2586 (1971).
153. F. P. Colonna, G. Distefano, M. Guerra, D. Jones, and A. Modelli, *J. Chem. Soc. Dalton*, No. 12, 2037 (1979).
154. K. Volka, P. Adamek, I. Stibor, and Z. Ksandr, *Spectrochim. Acta A*, **33A**, 241 (1977).
155. A. P. Ebdon, T. N. Huckerby, and F. G. Thorpe, *Tetrahedron Lett.*, No. 31, 3921 (1971).
156. D. Doddrell, K. G. Lewis, C. E. Mulquiney, W. Adcock, W. Kitching, and M. Bullpitt, *Aust. J. Chem.*, **27**, 417 (1974).
157. L. Lunazzi, M. Tiecco, C. A. Boicelli, and F. Taddei, *J. Mol. Spectrosc.*, **35**, 190 (1970).
158. A. D. Coxen and K. A. McLauchlan, *Mol. Phys.*, **7**, 11 (1963).
159. P. W. Jennings, S. K. Reedler, J. C. Hurley, C. N. Caughlan, and G. D. Smith, *J. Org. Chem.*, **39**, 3392 (1974).
160. Y. Miura, T. Onodzuka, and H. Shibaki, *Chemotherapy (Tokyo)*, **7**, 415 (1959).
161. M. Shiiken, *Nippon Yakurigaku Zasshi*, **54**, 658 (1958).
162. Y. Tanaka, I. Iwai, Y. Yura, and K. Tomita, *Chem. Pharm. Bull. Tokyo*, **8**, 252 (1960).
163. H. Sumi, Y. Tanaka, and Y. Kondo, *Takamine Kenkyusho Nempo*, **10**, 240 (1958). *Chem. Abs.*, **55**, 4861b (1961).
164. K. Tanaka, *J. Biochem. (Tokyo)*, **50**, 102 (1961); *Chem. Abs.*, **56**, 47746b (1962).
165. H. Sumi and K. Nakamura, *Takamine Kenkyusho Nempo*, **10**, 247 (1958). *Chem. Abs.*, **55**, 4861c (1961).