SYNTHESIS AND PROPERTIES OF 1,6-DIOXASPIRO[4.4]NONANE AND ITS DERIVATIVES (REVIEW)

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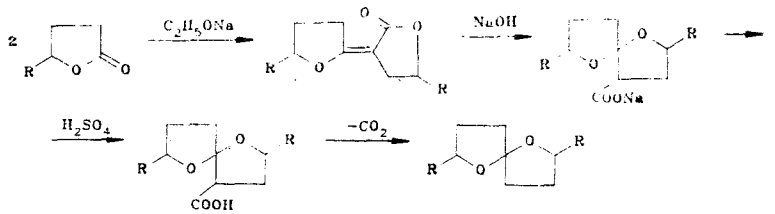
Data on methods of synthesis and the chemical properties of 1,6-dioxaspiro-[4.4]nonane and its derivatives are correlated.

In recent years, the chemistry of spiro compounds has undergone intensive development. A particularly large number of studies dealing with the isolation of spiroketal structures from natural sources and the establishment of their stereochemistry by modern spectral methods have been published, and original methods for the synthesis of natural spiroketals have been proposed. It has been shown that they have a broad spectrum of biological activity. Thus, natural spiroketals display antibiotic, anti-anaphylactic [1], antiphlogistic [2], and antispasmolytic [3] activity. In addition, they are used as catalysts in the manufacture of polymers [4], as attractants for bark beetles [5], and to accelerate processes involved in the combustion of solid rocket fuel [6]. Despite the great interest of chemists in such compounds and the constantly increasing number of publications in this area, there is only one review on 1,6-dioxaspiro[4.4]nonanes, which was published in 1959 [7]. Our review encompasses the literature up to 1984.

1. METHODS OF PREPARATION

1.1. Synthesis from Aliphatic Compounds and from γ-Lactones

1,6-Dioxaspiro[4.4]nonane and its dimethyl and diethyl homologs were first obtained by Fittig [8, 9] starting from lactones of γ-hydroxy carboxylic acids. The synthesis of these compounds included the condenstation of two molecules of the lactone in the presence of sodium ethoxide to give a dilactone, conversion of the latter to the sodium salt of a spiroketal acid by heating with a concentrated solution of sodium hydroxide, and decarboxylation of the resulting acid by refluxing with water or a dilute mineral acid:



R=H, CH_3, C_2H_5

The yields of the dimethyl- and diethylspiroketal reached 80%, whereas the unsubstituted spiroketal was obtained in lower yield as a consequence of partial cleavage of the butyrolactone and the formation of a hydroxybutyric acid salt. A spiroketal from butyrolactone and its dimethyl derivative from valerolactone were synthesized 10 years later by the same method (in the presence of diethylzinc) [10]. This method was also used for the preparation of spiroketals from α-substituted γ-lactones [11].

Volhard [12] proposed a new method for the preparation of such structures starting from aliphatic γ,γ'-dihydroxy ketones. He obtained diallylacetone dihydrobromide from diallylacetone by the action of hydrobromic acid, and 2,7-dimethyl-1,6-dioxaspiro[4.4]nonane was isolated by refluxing it with potassium carbonate solution:

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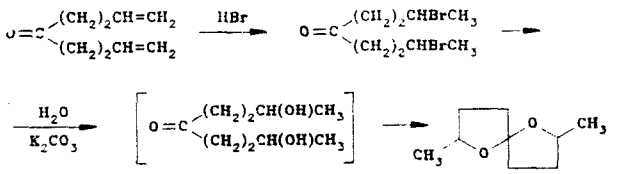
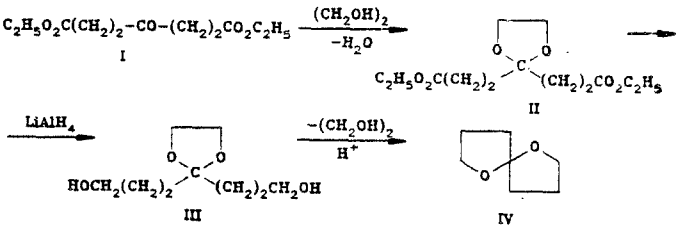
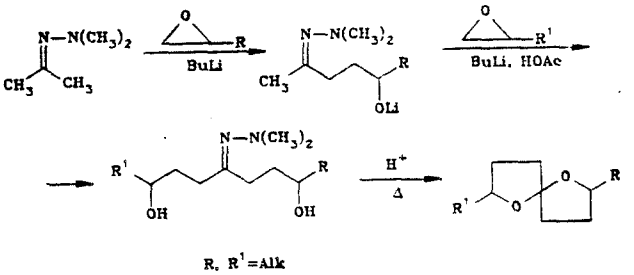


A method for the preparation of spiroketals from keto dicarboxylic acid diesters was later developed [13]:

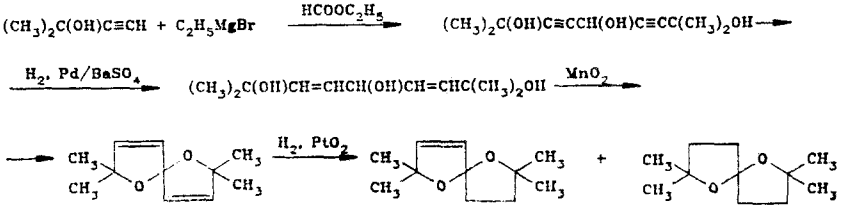


A simple method for the preparation of substituted spirononanes on the basis of acetone dimethylhydrazone and oxiranes was proposed in 1983 [14, 15]:

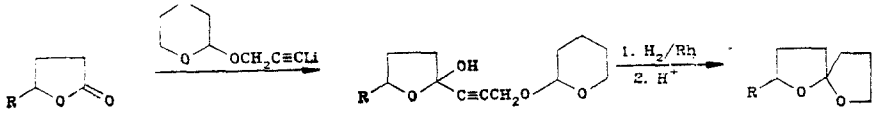


R, R^1=Alk

The one-step synthesis of spiroketals by oxidation of heptane-1,7-diol with lead tetraacetate in refluxing benzene in the presence of calcium carbonate was realized in 1965-1969 [16, 17]. However, because of the difficulties involved in the isolation of the spiroketals from the mixture of oxidation products, the yields of the desired products were less than 30%. The enantioselective synthesis of chalcogran from D-glucose [18, 19], as well as from the (S)-(−)-bromo epoxide [20], was accomplished by cyclization of the dihydroxy ketone. Unsaturated spiroketals that are present in products of plant origin [21, 22, 24-28] were synthesized by cyclization of alkenyl dihydroxy ketones [21-23]:



The structure of the principal aggregation-sex pheromone which is produced by male bark beetles of the species *Pityogenes chalcographus* was recently established [5]. This pheromone was isolated and identified as a mixture of isomers of 2-ethyl-1,6-dioxaspiro-[4.4]nonane (V) and was named chalcogran. The high biological activity of chalcogran as an attractant for bark beetles which feed on the Norwegian spruce was confirmed by field tests [5, 29]. A number of syntheses of chalcogran have been described [18-20, 23, 30-39]. A preparative method for the synthesis of chalcogran and its homologs based on the reaction of lithium salts of protected alkynols with equimolar amounts of lactones and subsequent hydrogenation, acid-catalyzed hydrolysis, and cyclization can be considered to be extremely efficient [37, 40, 41]:

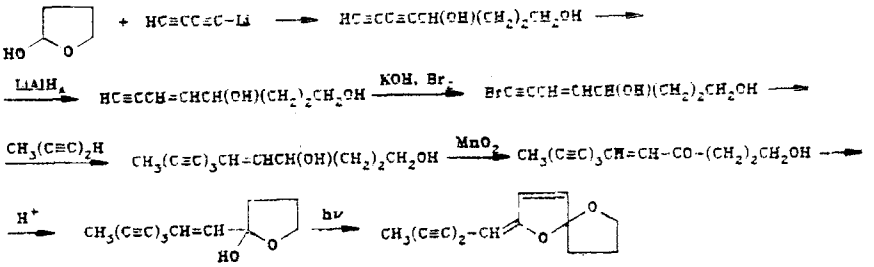


V

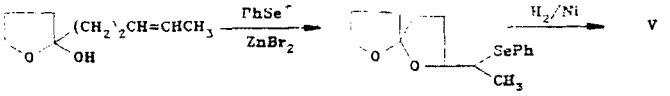
R=C_2H_5

A series of homologs of chalcogran was obtained in rather high yields by this method. The synthesis of 2,2,7,7-tetramethyl-1,6-dioxaspiro[4.4]non-3-ene, which was obtained in 42% yield from γ,γ-dimethyl-γ-butyrolactone and the lithium salt of the tetrahydropyranyl ether of 2-methyl-3-butyn-2-ol with subsequent hydrogenation over $Pd/CaCO_3$, was presented in [23]. 7-Methyl-1,6-dioxaspiro[4.4]nonanylacetic (exogonic) acid and its methyl ester (28% yield) were obtained by the same method from the lithium salt of (carboxymethyl)-γ-butyrolactone.

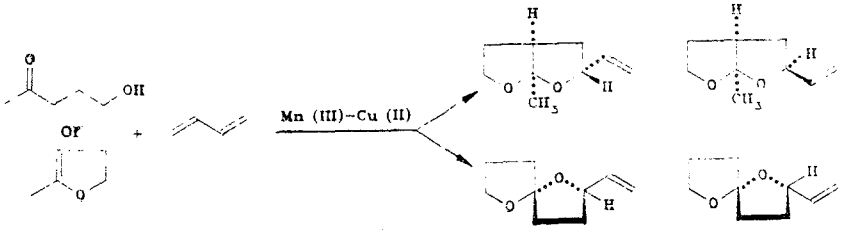
A model synthesis of enol ethers of spiroketals [43-47] on the basis of 2-hydroxytetrahydrofuran via the following scheme was developed to confirm the structures of a large group of polyyne compounds [42-79] from natural sources:



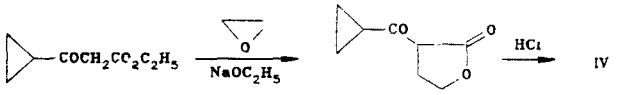
A method for the preparation of spiroketals by intramolecular cyclization of a hemiacetal through selenium-containing derivatives was proposed in [80]:



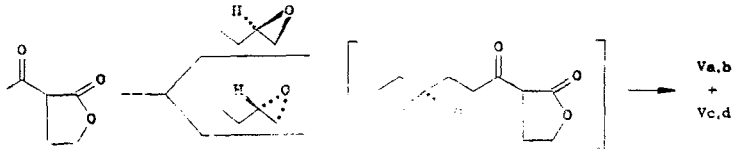
Spiroketal structures, together with condensed structures, were obtained in the oxidative addition to butadiene of acetopropyl alcohol or dihydro-α-methylfuran under the influence of the $Mn(OAc)_3$—$Cu(OAc)_2$ oxidizing system [81]:



An original method for the synthesis of spiroketal IV from ethyl 3-cyclopropyl-3-oxopropionate in 58% yield was proposed in 1956 [82]:

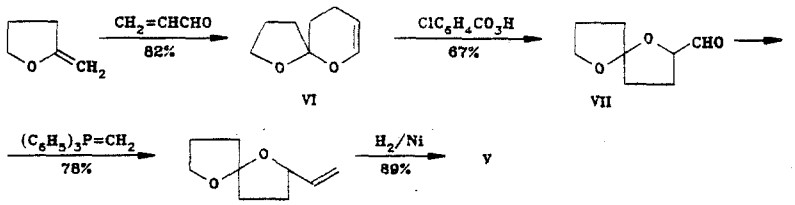


The Va, b (2R,5RS) and Vc, d (2S,5RS) diastereomers of chalcogran were obtained as the key products by alkylation of the dianion of α-acetyl-γ-butyrolactone with optically active epoxybutanes [30, 31, 83]:

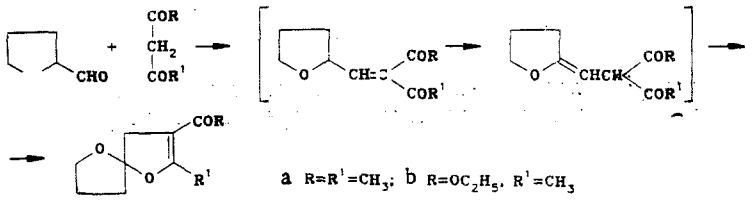


1.2. Synthesis from Tetrahydrofuran Derivatives

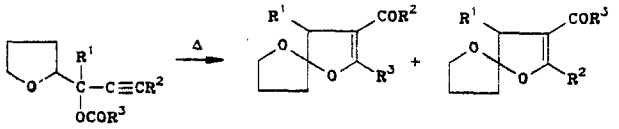
A method based on Diels—Alder condenstation between 2-methylenetetrahydrofuran and acrolein with subsequent oxidation of the resulting spiroketal VI to the corresponding carboxy aldehyde VII has proved to be quite successful [34, 38]:



The previously unknown substituted 1,6-dioxaspiro[4.4]non-2-enes were obtained by condensation of tetrahydrofurfural with acetylacetone and acetoacetic ester [84, 85]:

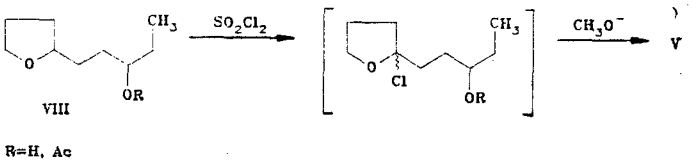


The maximum yield (65%) was achieved when a mixed catalyst, viz., piperidine or β-alanine with acetic acid, was used. Similar compounds in even higher yields (up to 70%) were obtained [86, 87] by thermal isomerization of propargyl esters of the tetrahydrofuran series. The reaction was carried out on quartz in a flow-type reactor at 500°C in an inert gas stream. It was shown that both acetates and benzoates in the vapor phase undergo isomerization to substituted 1,6-dioxaspiro[4.4]non-2-enes:



R^1=H, CH_3; R^2=CH_3, C_4H_9, C_6H_5; R^3=CH_3, C_6H_5

Tetrahydrofuran alcohols VIII were the key compounds for the synthesis of chalcogran proposed by Torgov and coworkers [88]. The yield of chalcogran from VIII was 57%.

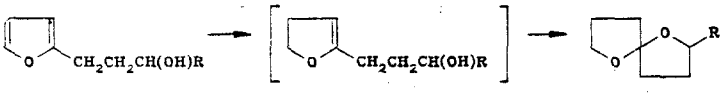


R=H, Ac

1.3. Synthesis from Furan Compounds

1.3.1. Catalytic Hydrogenation. 1,6-Dioxaspiro[4.4]nonane (IV) was detected for the first time in the products of hydrogenation of furylacrolein in 1934 [89, 90]. Hydrogenation was carried out on Raney nickel at 160°C and atmospheric pressure, and the yield of the spiroketal did not exceed 33%. It was later established [91] that 1,6-dioxaspiro[4.4]nonane and its 2-methyl homolog are formed in better yields (38-54%) in the hydrogenation of 1-furyl-3-propanol and 1-furyl-3-butanol over nickel on kieselguhr than in the case of hydrogenation of the corresponding unsaturated furan oxo compounds under the same conditions.

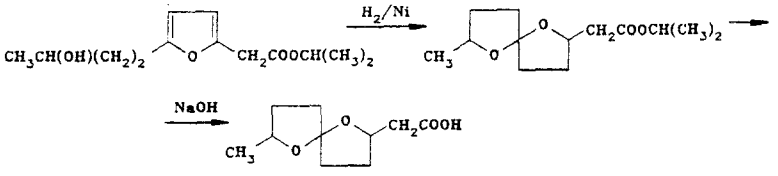
The formation of 2-methyl- and 2-(α-furylethyl)-1,6-dioxaspiro[4.4]nonane was noted in [92] in the hydrogenation of furfurylideneacetone and difurfurylideneacetone with a copper–chromium catalyst; the yields of spiroketals ranged from 15 to 25%. A number of homologs of 1,6-dioxaspiro[4.4]nonane were isolated in 30-40% yields in the hydrogenation of furan unsaturated alcohols in the liquid phase on a Raney nickel–aluminum catalyst [93-95]. 3-Methyl- and 3-ethyl-1,6-dioxaspiro[4.4]nonanes were obtained in 12-20% yields from the products of hydrogenation of α-alkyl-β-furylacroleins on a copper–aluminum catalyst. The following reaction mechanism was proposed in a study of the formation of spiroketal structures [91, 96, 97]:



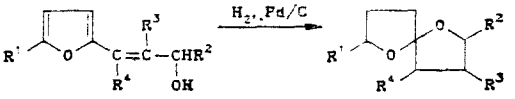
R=Alk

The experimental data on the formation of spirans in higher yields in the hydrogenation of furan alcohols than in the hydrogenation of aldehydes and ketones served as a basis for this assumption. In addition, the scheme of the formation of acetopropyl alcohol in the hydrogenation–hydration of 2-methylfuran proposed in [98] was taken into account. Ponomarev et al. synthesized 1,6-dioxaspiro[4.4]nonane derivatives by hydrogenation of various furan alcohols [7, 96, 97, 99-109]. It was established that, like primary and secondary furan alcohols that contain a hydroxy group attached to the third carbon atom of the side chain (γ-furylalkanols), tertiary γ-furylalkanols undergo cyclization with the formation of gem-disubstituted spiroketals in 20-78% yields when they are hydrogenated in the presence of nickel catalysts. The authors showed that the formation of homologs of 1,6-dioxaspiro[4.4]-nonane depends on the structure of the starting alcohol and the nature of the catalyst [104]. The following dependence of the yields of spiroketals in the hydrogenation of γ-furylalkanols on the nature of the catalyst was observed: nickel on kieselguhr >5% Ru/C > Raney nickel. The structure of the side chain of the furan alcohol has an even greater effect on the yields of these products. The yields of 1,6-dioxaspiro[4.4]nonane homologs from tertiary γ-furyl-alkanols are higher than those from secondary γ-furylalkanols; however, bulky substituents attached to the third carbon atom in the side chain hinder cyclization, and the spiroketal is formed in 4% yield. The yields of 1,6-dioxaspiro-[4.4]nonane homologs increase significantly in the hydrogenation of tertiary γ-furylalkanols with alkyl substituents attached to the first (from the ring) carbon atom of the side chain; in a number of cases the spiroketals are the chief reaction products. It has been assumed [104] that the presence of a branched side chain attached to the first (from the furan ring) carbon atom, by hindering hydrogenation of the double bond between the ring C_2 and C_3 atoms, creates favorable conditions for the formation of the intermediate 4,5-dihydrofuran compound that is necessary for the subsequent cyclization.

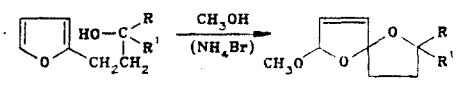
The catalytic hydrogenation of furan compounds has been successfully used for the synthesis of a number of natural spiroketals. Thus, Dedek et al. [110, 111] were able to accomplish the synthesis of exogonic acid by hydrogenation of isopropyl 5-(3-hydroxybutyl)-2-furylacetate over Raney nickel (160°C, 7MPa) with subsequent alkaline saponification:



Among the numerous methods for the synthesis of chalcogran and its analogs, the hydrogenation of furan compounds under mild conditions (at room temperature and atmospheric pressure) over 10% Pd/C can also be considered to be quite successful [32]. The yields (20-53%) vary as a function of the substituents.



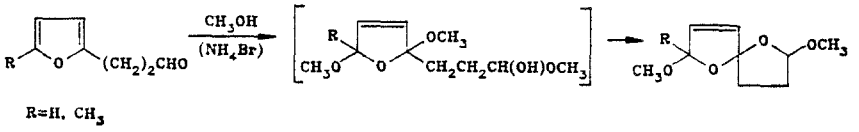
1.3.2. Electrolytic Alkoxylation of γ-Furylalkanols and γ-Carbonyl-Containing Furan-Compounds. On the basis of the Clauson-Kaas method, Ponomarev et al. [112-118] developed a new method for the preparation of 1,6-dioxaspiro compounds by electrolytic alkoxylation of γ-furylalkanols. The authors started from the assumption that, because of the spatial closeness of the hydroxy group in the side chain to the furan ring in such alcohols, in addition to alkoxylation, intramolecular cyclization is extremely likely:



R, R¹ = Alk

It was established that primary, secondary, and tertiary γ-furylalkanols are converted to the corresponding 2-methoxy-1,6-dioxaspiro[4.4]non-3-ene derivatives in the case of electrolysis of solutions of them in methanol [114-116]. The yields reached 76% of the theoretical values. In a study of the alkoxylation conditions it was shown [117] that the presence of a methyl group in the 5 position of the furan ring in the alcohols does not have an appre-

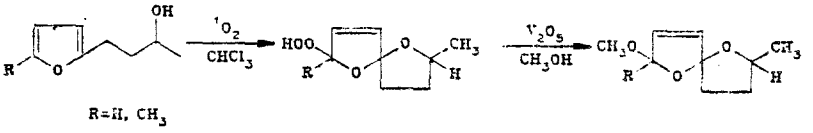
ciable effect on the formation of 2-methyl-2-methoxy-1,6-dioxaspiro[4.4]non-3-enes and that an accumulation of alkyl groups in the aliphatic chain, particularly the presence of a gem-dimethyl group attached to the first (from the furan ring) carbon atom of the side chain, significantly facilitates cyclization under electrolysis conditions. The yields of polyalkyl-substituted 2-methoxy-1,6-dioxaspiro[4.4]non-3-enes reached 95%. Similarly, a number of 2-ethoxyspirononenes were obtained in 76-83% yields in the electrolysis of solutions of primary, secondary, and tertiary γ-furylalkanols in ethanol [118]. Makrushina and Shulyakovskaya studied the electrolytic alkoxylation of γ-carbonyl-containing furan compounds [119, 120]. It was shown that under electrolysis conditions aldehydes and ketones of the furan series behave differently. The electrolytic methoxylation of furan aldehydes led to 2,7-dimethoxy-1,6-dioxaspiro[4.4]non-3-enes in 72-75% yields.



The authors assume that the hemiacetal of the furan aldehyde is formed as an intermediate during the reaction. The electrolytic methoxylation of furan ketones led to 2,5-dimethoxy-2,5-dihydrofuryl-3-butanones; the formation of spiro compounds was not observed.

In addition to the electrolytic alkoxylation of furan compounds, chemical alkoxylation, which has been successfully used to prove the structures of natural spiroketals isolated from various higher plants, has been used for the synthesis of 1,6-dioxaspiro compounds [44, 47]. Chemical alkoxylation has also been used for the synthesis of enol ethers of spiroketals that have sulfur-containing groups as an additional function [45].

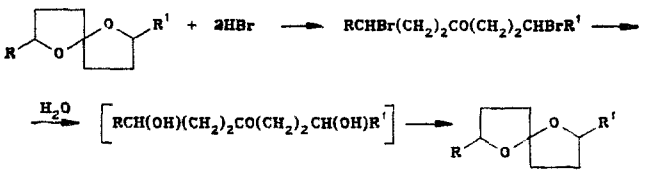
A photooxidative analog of the Clauson-Kaas reaction was proposed in 1982 [121] for the conversion of furan compounds to alkoxydihydrofurans. A mixture of diastereomers of 2-methoxy-1,6-dioxaspiro[4.4]non-3-enes, which are structural units for many natural compounds, was obtained from 4-(2-furyl)-2-butanol in good yield.



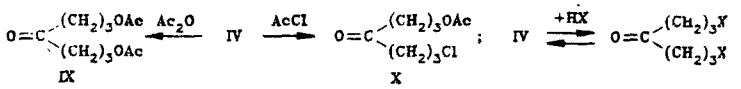
2. PROPERTIES OF 1,6-DIOXASPIRO[4.4]NONANE AND ITS DERIVATIVES

With respect to their chemical structures, 1,6-dioxaspiro[4.4]nonane (IV) and its homologs are intramolecular cyclic spiroketals of γ,γ'-dihydroxy ketones. 1,6-Dioxaspiro[4.4]-nonane is a molecule that has activity without the presence of an asymmetric atom. The five-membered rings of spiroketal IV lie in mutually perpendicular planes, and the relative orientation of the oxygen atoms in the rings (to the right and left of the spiral) is responsible for the existence of optical antipodes; this was confirmed experimentally by the asymmetric synthesis of optical antipodes by hydrogenation of furylacrolein over nickel applied to an optically active support (d- and l-quartz) [122-123] and 1-(2-furyl)-3-butanol over Raney nickel modified by D-tartaric acid [124].

It has been established [8, 11, 12, 90, 91, 125] that 1,6-dioxaspiro[4.4]nonane and its alkyl derivatives react with concentrated hydrohalic acids to give dihalides, which are readily hydrolyzed to dihydroxy ketones; the latter are converted to the starting spiroketals as a result of spontaneous intramolecular cyclization to the starting spiroketals:

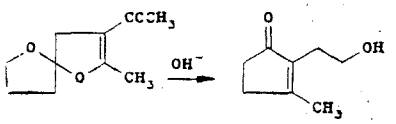


Ketone IX was obtained in 43% yield by acetylation of spiroketal IV with acetic anhydride. Acetylation of the same compound with acetyl chloride led to 1-acetoxy-7-chloro-4-heptanone (X) in 62% yield [126]. Products of acidolysis of spiroketal IV by organic acids (HX) were isolated in quite good yields and were characterized.



X=HCOO, CH_3COO, $ClCH_2COO$

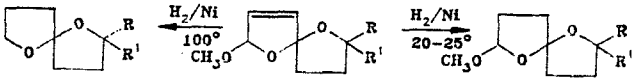
The experimental facts under consideration are in good agreement with the general mechanism of acidic hydrolysis of acetals. Like ordinary ketals, spiroketals with saturated carbon bonds are characterized by stability in alkaline media [8]. As regards the carbonyl derivatives of 1,6-dioxaspiro[4.4]non-2-enes, heating to 45°C with 15% sodium hydroxide solution led to 2-(2-hydroxyethyl)-3-methyl-2-cyclo-1-pentenone in quantitative yield [84]:



Butyrolactone was obtained in the oxidation of 1,6-dioxaspiro[4.4]nonane with nitric acid, whereas oxidation of the simplest spiroketal with potassium permanganate in an aqueous medium led to succinic acid in good yield [7]. Spiroketals are quite active reducing agents. They react with an ammoniacal solution of silver oxide with gentle heating to give a silver mirror [7].

When a solution of spiroketal IV in benzene is refluxed with powdered sodium, it is reduced to the γ-tetrahydrofurylalkanol in 48% yield [126]. Hydrogenolysis of saturated spiroketals was detected under severe hydrogenation conditions. Thus, spiroketal IV at 200°C and 10-20 MPa undergoes partial reduction in the presence of nickel on kieselguhr to give tetrahydrofurylpropanol in 39% yield [89]. 2-Methyl-1,6-dioxaspiro[4.4]nonane forms a mixture of octane-1,4,7-triol (47.8%) and tetrahydrofuryl-3-butanol (18.2%) when it is hydrogenated under pressure (20 MPa, 200°C, nickel on a zeolite) in the presence of water and a small amount of formic acid. In the presence of copper–chromium catalyst under the same conditions 56.2% octane-1,4,7-triol and 16.2% tetrahydrofuryl-3-butanol are formed [127].

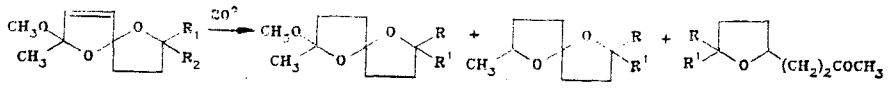
The hydrogenation of polyalkyl-substituted 2-methoxy- and 2,7-dimethoxy-1,6-dioxaspiro-[4.4]non-3-enes in the presence of heterogeneous and homogeneous rhodium catalysts has been investigated [3, 114-120]. The hydrogenation of unsaturated spiroketals XI under pressure of 10 MPa at room temperature in the presence of Raney nickel led to the corresponding methoxyspiroketals XII in 70-89% yields. Not only reduction of the ring double bond but also splitting out of the methoxy group to give saturated spiroketals XIII (54-69% yields) were observed at a high temperature (100°C) [118-120].



XIII XI XII

R, R' = Alk

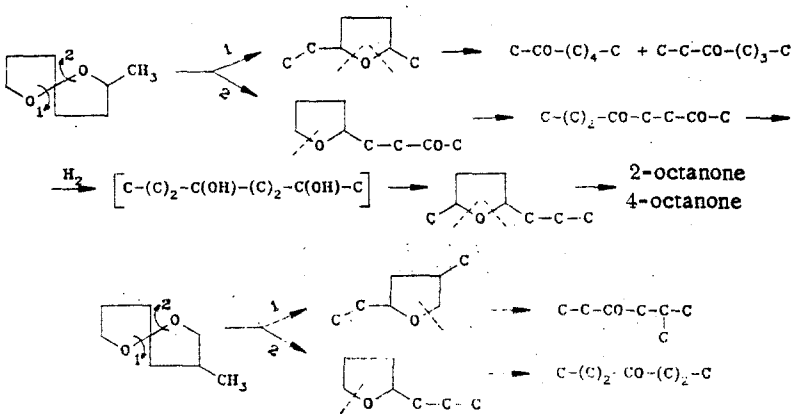
The hydrogenation of spiro-3-nonene derivatives that contain not only a methoxy group but also a methyl group in the 2 position leads, even at room temperature in the presence of Raney nickel, to a mixture of products [117]:



R, R' = Alk

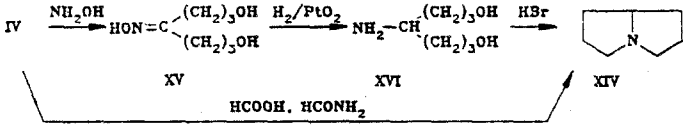
The corresponding saturated 2-methoxy-1,6-dioxaspiro[4.4]nonanes were obtained in quantitative yields in the hydrogenation of polyalkyl-substituted 2-methoxy-1,6-dioxaspiro[4.4]non-3-enes under mild conditions in the presence of homogeneous catalysts based on rhodium complexes. Splitting out of the methoxy group was not observed. A catalyst based on a complex of rhodium with fluorescein was found to be the most effective [3].

It is known [128] that 2- and 3-methyl-1,6-dioxaspiro[4.4]nonanes in the vapor phase on platinized carbon at 300-320°C undergo the following transformations:

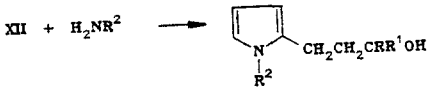


It should be noted that, in addition to the final reaction products, viz., aliphatic ketones and diketones, intermediates, viz., tetrahydrofuran homologs and a tetrahydrofuran ketone, were isolated. The behavior of the simplest spiroketal (IV) in the vapor phase on pumice and various forms of SiO_2 at 340-360°C has been examined. Spiroketal IV remains unchanged on pumice, whereas when silicon dioxide is used, IV undergoes partial conversion to β-(tetrahydro-2-furyl)propionaldehyde and 3-(4,5-dihydro-2-furyl)-1-propanol [129].

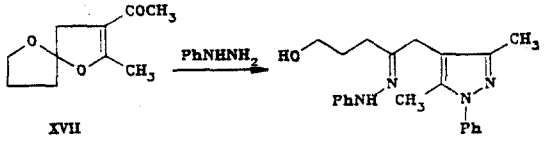
Pyrrolizidine (XIV) (6% yield) was isolated when spiroketal IV was treated with an equimolar mixture of concentrated formic acid with formamide. The same compound was obtained in higher overall yield (36%) by a three-step synthesis through oxime XV with subsequent hydrogenation on Adams' catalyst and treatment of the resulting amino diol XVI with hydrobromic acid [126]:



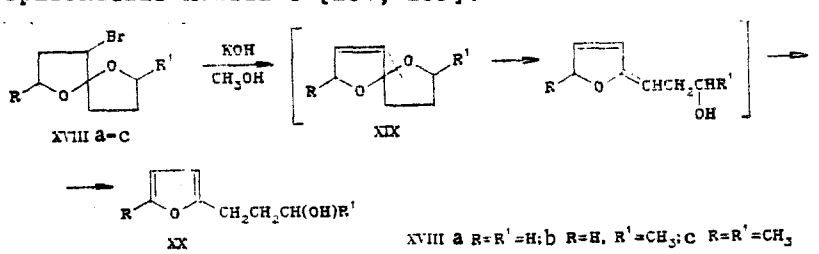
N-Substituted 1-(2-pyrrolyl)-3-alkanols were obtained in 42-98% yields in the reaction of 2-methoxy-1,6-dioxaspiro[4.4]nonanes XII with primary amines [130].



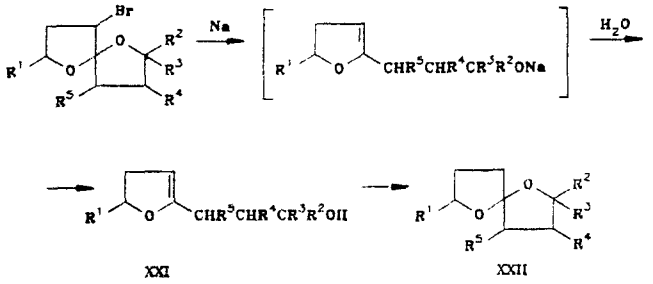
3,5-Dimethyl-4-(5-hydroxy-2-oxopentyl)-N-phenylpyrazole phenylhydrazone was obtained in 42% yield as a result of the reaction of spiroketal XVII with phenylhydrazine at room temperature [84]:



In [131-139] it was shown that the bromination of 1,6-dioxaspiro[4.4]nonane with dioxane dibromide takes place in the 4 and 9 positions. It was subsequently observed that mono- and dibromo derivatives of the spiroketal are also formed in rather good yields (58-78%) upon reaction with bromine in the presence of calcium carbonate [134]. Instead of the expected spirononenes XIX, (hydroxyalkyl)furans XX were isolated in the dehydrobromination of monobromo-substituted spiroketals XVIIIa-c [134, 135].

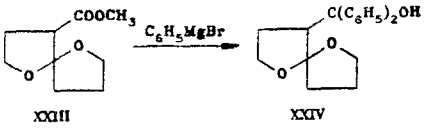


The only reaction products in the dehydrobromination of monobromo derivatives of 1,6-dioxaspiro[4.4]nonanes with several alkyl substituents were the corresponding spirononenes [135]. Their yields reached 83%. The peculiarities of the chemical structures (internal two-ring ketals) of 1,6-dioxaspiro[4.4]nonane derivatives have also been reflected in the reaction of monobromo-substituted 1,6-dioxaspiro[4.4]nonanes with sodium metal. The expected 3-(4,5-dihydro-2-furyl)propanol could be isolated in 70% yield only in the case of the simples bromospiron, viz., 4-bromo-1,6-dioxaspiro[4.4]nonane (XVIIIa) [136].

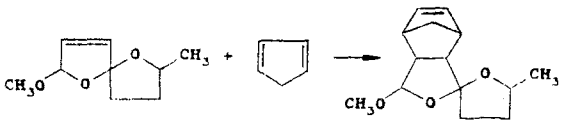


In the action of sodium on monobromo-substituted 1,6-dioxaspiro[4.4]nonanes with several alkyl substituents the principal reaction products were the corresponding spiroketals XXII (60-70% yields). It was assumed that they are formed from intermediate (dihydrofuryl)alkanols XXI, traces of which were detected in the reaction products by means of IR spectroscopy.

Under the conditions of the Grignard reaction in the case of equimolar amounts of the reagents or an excess of the organomagnesium compound [137] 1,6-dioxaspiro[4.4]nonane (IV) and its 2-methyl homolog react only with one molecule of RMgX to give the corresponding 3-(2-R-tetrahydro-2-furyl)propanols [138]. The reactivities of the spiroketals in the reaction with Grignard reagents depend on the nature of the substituents. Thus, for example, when a methoxycarbonyl group was present, cleavage of the acetal bond of spiroketal XXIII was not observed, and tertiary alcohol XXIV was isolated in 72% yield [139]:

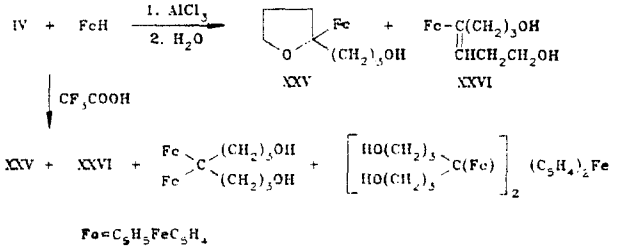


Methoxy-substituted 1,6-dioxaspiro[4.4]non-3-enes have been used as dienophiles in the diene synthesis. The reaction of 2-methoxy-7-methyl-1,6-dioxaspiro[4.4]non-3-ene with various dienes in absolute toluene at 130-160°C was realized. The yields of adducts ranged from 20 to 48% [140].



Using dimethyl sulfoxide, which is known for its high isomerizing ability, as the solvent, Karakhanov et al. [84] were able to obtain 2-methyl-3-acetyl-5-(3-hydroxypropyl)furan from spiroketal XVII by refluxing in an inert gas atmosphere.

It was recently shown that 1,6-dioxaspiro[4.4]nonane (IV) reacts with ferrocene in the presence of Lewis acids [141]. The pathway of this acid-catalyzed reaction depends on the nature of the catalyst. When boron trifluoride etherate or aluminum chloride was used as the catalyst, the reaction proceeded with the formation of 2-ferrocenyl-2-(3-hydroxypropyl)-tetrahydrofuran (XXV) (55-89% yields). The authors feel that diol XXVI is formed only at the end of the process, when the reaction mixture is treated with ice water, as a consequence of reaction of the principal product (XXV) with the hydrochloric acid liberated in the hydrolysis of $AlCl_3$. The reaction with ferrocene in the presence of trifluoroacetic acid led to a mixture of ferrocene derivatives. The isolated ferrocene derivatives are used as components for the direct introduction of ferrocenyl groups into polyurethane systems and as catalysts for the acceleration of the combustion of solid rocket fuel [6].



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SYNTHESIS AND THREE-DIMENSIONAL STRUCTURES OF 2-(2-FURYL)-ACRYLONITRILES

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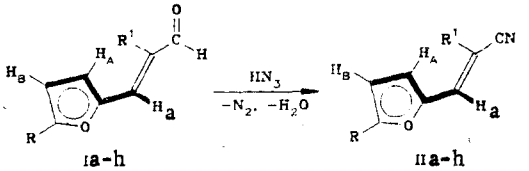
Conditions for carrying out the Schmidt reaction that make it possible to obtain β-(2-furyl)acrylonitriles in high yields were found. It was shown by PMR and IR spectroscopy that the furylacrylonitriles obtained have an E-s-cis configuration.

In a previous communication [1] we described the conditions for the synthesis of 2-cyanofurans from the corresponding 2-formylfurans via the Schmidt reaction. These conditions were found to be unsuitable for the synthesis of furylacrylonitriles IIa-h from furylacroleins Ia-h because of pronounced resinification of the reaction mixtures. One can, however, avoid resinification if dioxonium perchlorate is introduced into the reaction mixture instead of $HClO_4$.



Ia-h IIa-h

R=H, CH_3, C_6H_5, 2,4,6-$C_6H_2Cl_3$, NO_2; R^1=H, CH_3

According to PMR data, starting furylacroleins I have an E configuration [2, 3]. We were interested in the peculiarities of the three-dimensional structures of the resulting nitriles IIa-h (Table 1).

The H_aR^1 spin-spin coupling constants (SSCC), which are 15.0-17.0 Hz (when R^1 = H) and 1.4-2.0 Hz (when R^1 = CH_3) (Table 2), constitute evidence for a trans orientation of these groups relative to the exocyclic double bond in IIa-h. Their IR spectra contain an absorp-

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