HETARYLFERROCENES (REVIEW)

G. A. Shvekhgeimer

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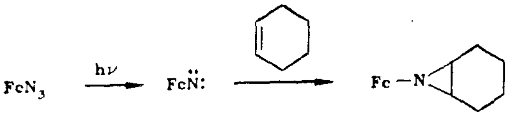
Data on the synthesis, transformations, and utilization of ferrocene derivatives that contain heterocyclic radicals bonded directly to the ferrocene fragment are correlated.

Compounds that contain ferrocenyl and heterocyclic radicals were described in 1951 [1] shortly after the production of ferrocene was reported [2]. By 1969 more than 40 reviews on the chemistry of ferrocene had been published [3]. Hetarylferrocenes were only mentioned in these publications. A review that was devoted entirely to hetarylferrocenes was published only in 1971 [4]. A paper [5] in which data on compounds that contain heterocyclic rings condensed with the ferrocene system was published later.

In the present review data from the start of 1989 regarding ferrocene derivatives that contain heterocyclic radicals are systematized; only compounds in which the ferrocenyl radical is bonded directly to any atom that enters into the heterocyclic ring are considered.

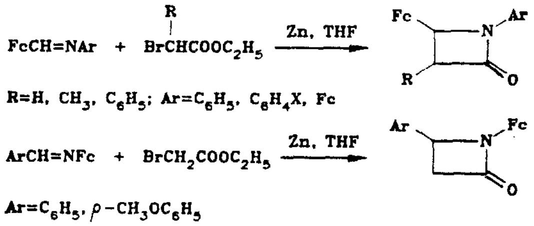
1. NITROGEN-CONTAINING HETARYLFERROCENES

A nitrene, which adds to cyclohexene to give the corresponding aziridine, is formed when ferrocenyl azide is heated or subjected to UV irradiation [6]:

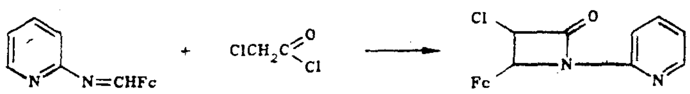


Here and subsequently Fc = $C_5H_5FeC_5H_4$ −, ferrocenyl

In 1969, Cuignet and co-workers [7] reported the synthesis of azetidine derivatives containing a ferrocenyl radical by means of a modified Reformatskii reaction:



3-Chloro-1-(2-pyridyl)azetidin-2-one was obtained by cyclocondensation of a ferrocenyl azomethine with chloroacetyl chloride [8]:



Nesmeyanov and co-workers were able to synthesize ferrocenylpyrroles that contain a ferrocenyl radical in any position of the pyrrole ring. 1-Ferrocenylindole is formed when bromoferrocene is treated with potassium tetra(1-indolyl)borate in the presence of Cu_2Br_2 [10], while a mixture of 1- and 3-ferrocenylindole is formed when it is treated with N-magnesiobromoindole [9].

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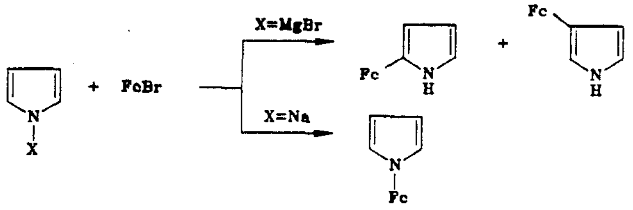
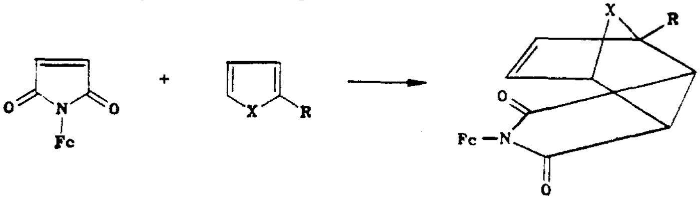
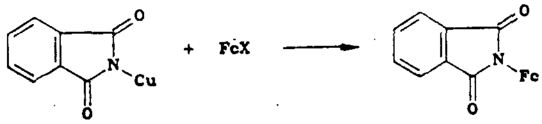


N-Ferrocenylmaleinimide, obtained from maleic anhydride and aminoferrocene, reacts stereospecifically with cyclic dienes to give endo adducts (demonstrating the steric effect of the Fc radical) [11]:



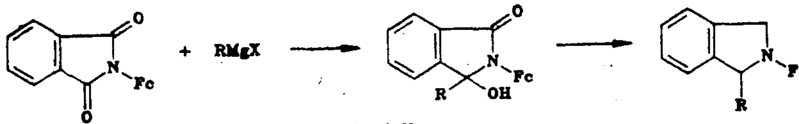
R=H, X=R=CH_2; C=C$(CH_3)_2$, O, C=CHFc, C=C(CH_3)Fc; R=CH_3,

N-Ferrocenylphthalimide can be synthesized starting from copper phthalimide and ferrocenylboric acid [12], chloromercuriferrocene [13], or iodo- or bromoferrocene [14-18]:



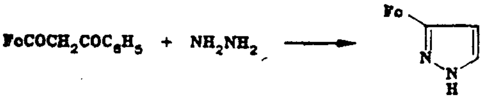
X=B$(OH)_2$, HgCl, I, Br

1,1'-Bis(phthaloimidoyl)ferrocene was obtained from phthalimide and 1,1'-dibromo- or 1,1'-diiodoferrocene in the presence of Cu_2O [18]. N-Ferrocenylphthalimide reacts with Grignard reagents to give hydroxy oxo compounds, which were reduced with lithium aluminum hydride to give dihydroisoindole derivatives [19]:

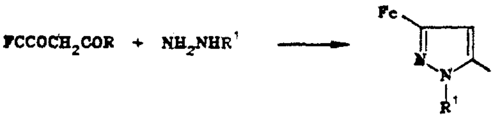


R=CH_3, C_2H_5, $C_6H_5CH_2$, C_6H_5

Among hetarylferrocenes, researchers have been most interested in pyrazole derivatives. This type of compound was synthesized for the first time by the reaction of a diketone with hydrazine in absolute ethanol [20]:

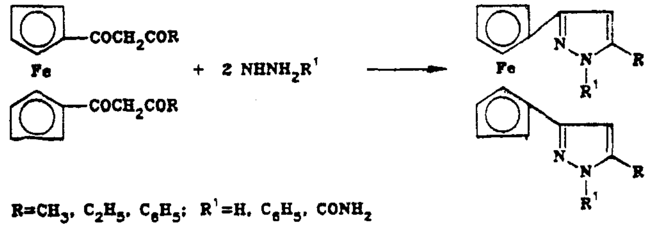


This reaction was subsequently extended to various hydrazine derivatives [21-24]. It was shown that of the two possible cyclization pathways, the one that is determined by the smaller degree of steric hindrance and the stability of the intermediately formed hydrazones is realized [24, 25]:



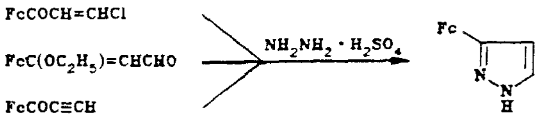
R=CH_3, Fc, R^1=H; R=CH_3, R^1=CH_3, C_6H_5, $C_6H_3(NO_2)_2$, $CONH_2$

The corresponding 1,1'-bis(3-pyrazolyl)ferrocenes are formed from ferrocene derivatives that contain two $COCH_2COR$ groupings [25, 26]:



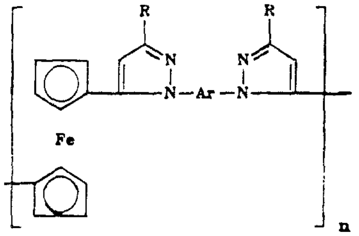
R=CH_3, C_2H_5, C_6H_5; R^1=H, C_6H_5, $CONH_2$

Similar bishetarylferrocenes are also formed when ferrocene derivatives that contain two $COCH_2COR$ groupings ($R = OH, OC_2H_5$) are refluxed with hydrazine in ethanol in the presence of CH_3COOH [27]. 3-Ferrocenylpyrazole or 1,1'-bis(3-pyrazolyl)ferrocene was synthesized by the reaction of $FcCOCH_2CHO$ with hydrazine sulfate or $Fc(COCH{=}CHONa)_2$ with hydrazine hydrate [28]. Ferrocenyl β-chlorovinyl ketone [28], 3-ethoxy-3-ferrocenylacrolein [29], and ferrocenyl ethynyl ketone [30] have also been used as starting compounds for obtaining 3-ferrocenylpyrazole:

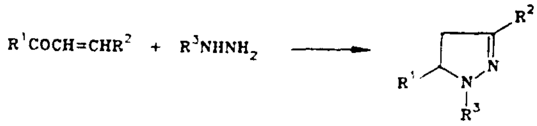


1-Ferrocenylpyrazole or 1-ferrocenyl-3,5-dimethylpyrazole was synthesized as a result of the direct hetarylation of ferrocene by the action of sodium derivatives of pyrazole or 3,5-dimethylpyrazole on ferricinium hexafluorophosphate [31].

The polycondensation of ferrocene derivatives that contain two $COCH_2COR$ groupings with dihydrazines proceeds readily with the formation of polyhydrazones, which on heating are converted to poly(ferrocenylpyrazoles) [32]:

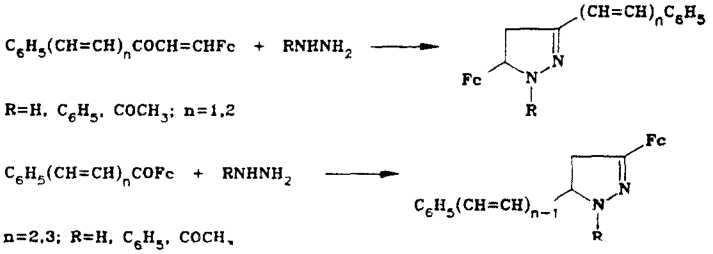


The reaction of ferrocenyl-containing unsaturated ketones $RCOCH{=}CHR^1$, which is usually carried out by heating a mixture of the components in ethanol in the presence of acetic acid, has been studied in rather great detail [33-38]:

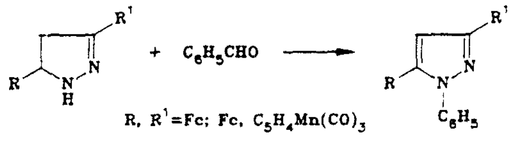


$R^1{=}H$, Ar, Fc, $C_5H_4Mn(CO)_3$; $R^2{=}Alk$, Ar, Fc, $C_5H_4Mn(CO)_3$; $R^3{=}H$, Ar, Fc

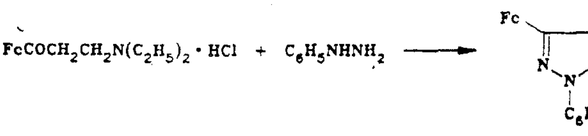
Nesmeyanov and co-workers investigated the reaction of $RNHNH_2$ with unsymmetrically substituted divinyl ketones that contain a ferrocenyl radical and established that cylization to imidazolines occurs with the participation of the double bond conjugated with the Fc radical. They explain this reaction pathway by the fact that the latter is a stronger electron donor than C_6H_5 [39]:



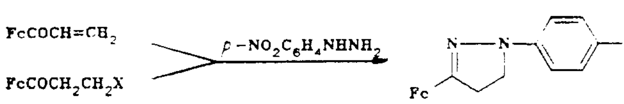
N-Phenylpyrazoles are formed by treatment of N-unsubstituted pyrazolines with benzaldehyde [40]:



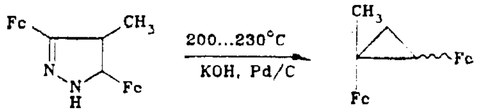
1-Phenyl-3-ferrocenylpyrazoline was synthesized by treatment of the corresponding Mannich base with phenylhydrazine [41]:



Ferrocenyl vinyl ketone or ferrocenyl β-haloethyl ketones can also be used to obtain ferrocenylpyrazolines [42]:

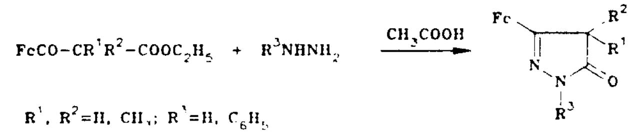


Ferrocenylpyrazolines are converted to ferrocenylcyclopropanes when they are heated in the presence of potassium hydroxide and Pd/C [43]:



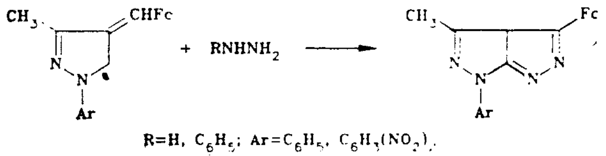
Ferrocenylpyrazolines are characterized by their IR [33, 41], PMR [33, 44], and mass spectra [45].

The corresponding ferrocenylpyrazolones were obtained as a result of the cyclocondensation of ethyl esters of ferrocenylglyoxylic acid [20] or its substituted derivatives [46] with hydrazine or phenylhydrazine:



R1, R2=H, CH3; R3=H, C6H5

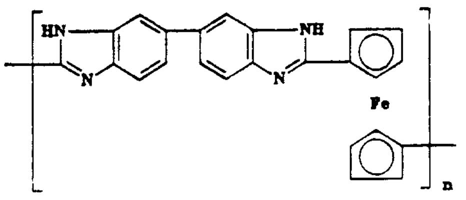
Compounds that contain two condensed pyrazoline rings are formed in the condensation of 1-aryl-3-methyl-4-ferrocenylmethylenepyrazol-5-one with hydrazine or phenylhydrazine [47]:



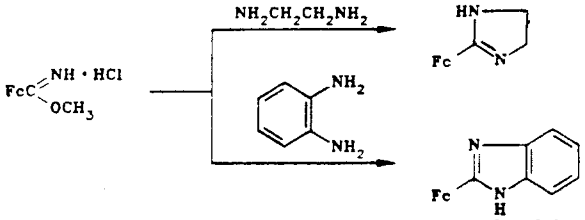
R=H, C6H5; Ar=C6H5, C6H4(NO2).

Direct hetarylation of ferrocene occurs in the reaction of ferricinium hexafluorophosphate with the sodium derivative of imidazole, and 1-ferrocenylimidazole is formed [31].

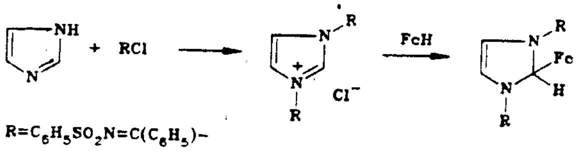
The polycondensation of ferrocene-1,1'-dicarboxylic acid with 3,3'-diaminobenzidine has been studied. This polycondensation gave the corresponding polymer [48]



2-Ferrocenylimidazoline or 2-ferrocenylbenzimidazole is formed in high yield in the condensation of methyl ferroceniminocarboxylate hydrochloride with ethylenediamine or o-phenylenediamine [49]:

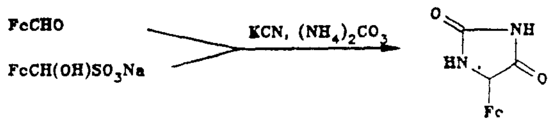


1,3-Bis(phenylsulfonylbenzimidoyl)-2-ferrocenyl-4-imidazoline was obtained by treatment with ferrocene of the salt formed in the reaction of imidazole with phenylsulfonylbenzimidoyl chloride [50]:

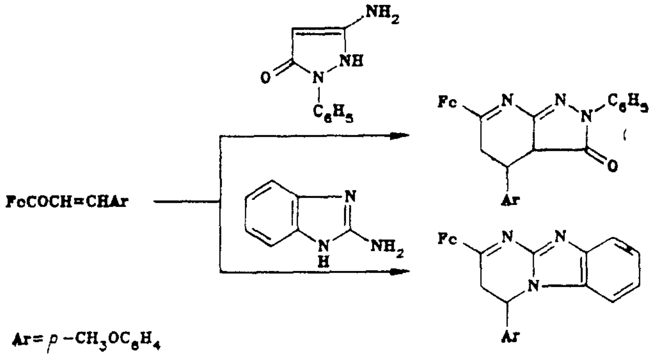


R=C6H5SO2N=C(C6H5)-

4-Ferrocenylhydantoin was synthesized by two methods: either from formylferrocene or from its bisulfite derivative [51, 53]:

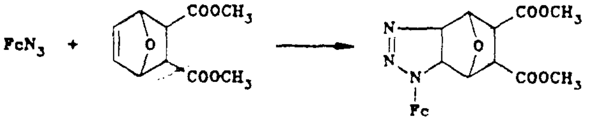


An interesting method for the synthesis of heterocyclic condensed systems that contain a pyrazole or imidazole ring consists in the reaction of ferrocenyl β-(p-methoxyphenyl)vinyl ketone with 3-amino-1-phenylpyrazol-5-one or with 2-aminobenzimidazole [54]:

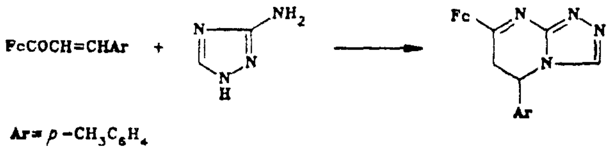


The method of direct hetarylation of ferricinium hexaphosphate with the sodium derivative of benzotriazole was used to obtain 1-ferrocenylbenzotriazole [31].

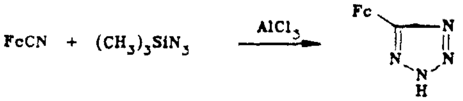
Ferrocenyl azide is capable of undergoing 1,3-dipolar cycloaddition to give the corresponding adduct [55]:



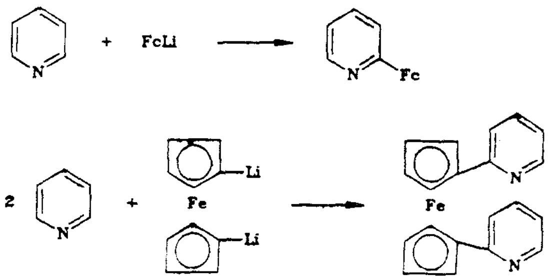
A triazolopyrimidine was obtained as a result of condensation of 3-amino-1,2,3-triazole with a chalcone of the ferrocene series [54]:



5-Ferrocenyltetrazole was synthesized by the reaction of cyanoferrocene with trimethylsilyl azide [56]:

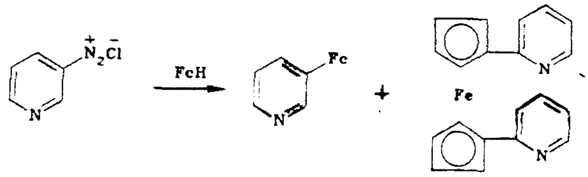


The mono- and dilithium derivatives of ferrocene react with pyridine to give, respectively, 2-pyridylferrocene and 1,1'-di(2-pyridyl)ferrocene [57, 58]:

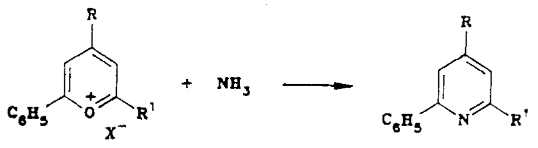


2-Pyridylferrocene was also synthesized by the reaction of 1,1'-ferrocenylenediboric acid with pyridine [58].

A mixture of 3-pyridylferrocene with a small amount of 1,1'-di(3-pyridyl)ferrocene is formed when a 3-pyridinediazonium salt is treated with ferrocene [57]:

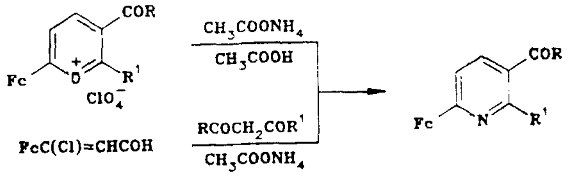


A number of derivatives of 2-pyridyl- and 4-pyridylferrocene were obtained on treatment of the corresponding pyrylium salts with an alcohol solution of ammonia [59, 60]:



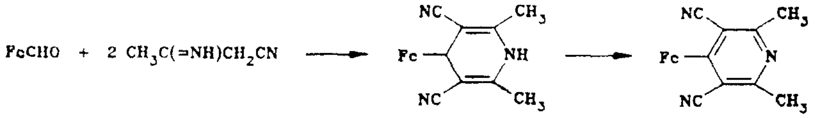
$R = C_6H_5$, $R^1 = Fc$; $R = Fc$, $R^1 = C_6H_5$; $X^- = ClO_4^-$, HSO_4^-, BF_4^-

Ammonium acetate can be used in place of ammonia to convert pyrylium salts to pyridine bases [61]. The same pyridine bases were obtained by the reaction of 3-chloro-3-ferrocenylacrolein with 1,3-diketones in the presence of ammonium acetate [62]:

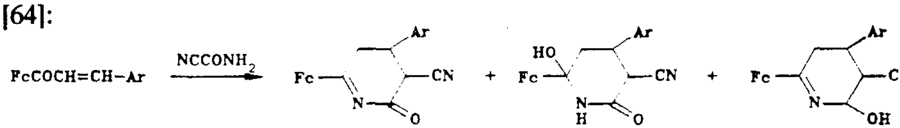


$R = R^1 = C_6H_5$, CH_3; $R = C_2H_5O$, $R^1 = CH_3$; $R - R' = -CH_2C(CH_3)_2CH_2-$

The reaction of formylferrocene with diacetonitrile gives a 1,4-dihydropyridine derivative which, by the action of chloranil, is converted to 3,5-dicyano-2,6-dimethyl-4-ferrocenylpyridine [63]:

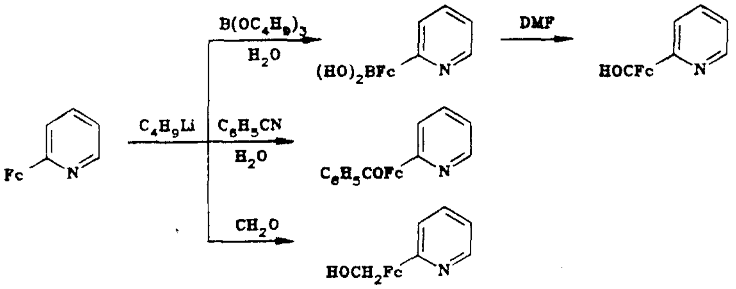


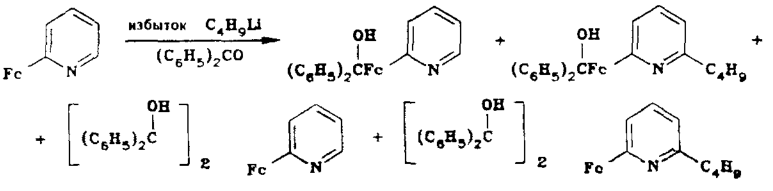
A whole gamut of hetarylferrocenes is formed on treatment of ferrocenylchalcones with cyanoacetamine in the presence of bases [64]:



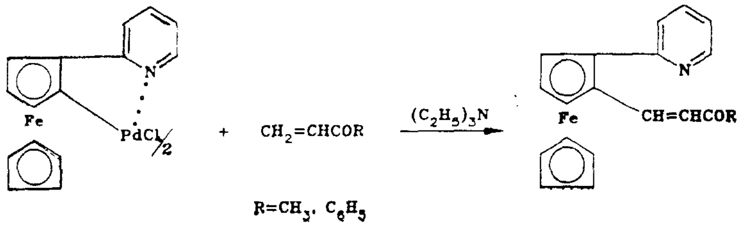
$Ar = C_6H_5$, $p-ClC_6H_4$

A number of interesting transformations were accomplished on the basis of the lithium derivative of 2-pyridylferrocene [65-67]:





The corresponding vinyl ethers were obtained by treatment of the palladium complex of 2-pyridylferrocene with methyl vinyl ketone or phenyl vinyl ketone [68]:



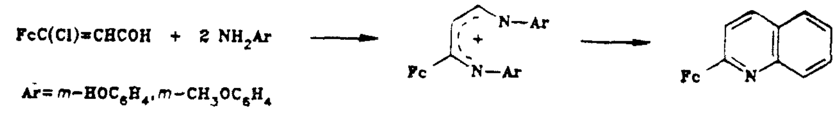
Decomposition of the ferrocene system is observed in the photolysis of 2-pyridylferrocene methiodide in an aqueous medium at pH > 7 [69, 70].

The reaction of chloroferrocene with the lithium derivative of piperidine leads to the formation of a mixture of products containing N-ferrocenylpiperidine [71].

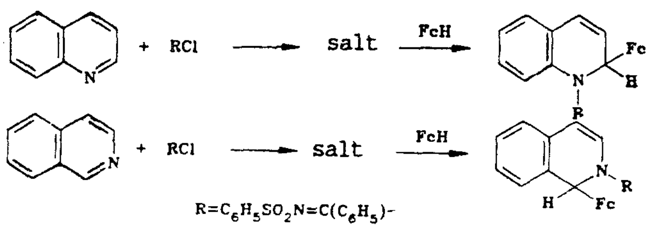
The hetarylation of the lithium derivative of ferrocene with quinoline to give 2-quinolylferrocene and 1,1'-di(2-quinolyl)ferrocene has been described [57].

The ferrocenyl radical was introduced into the 5 position of quinaldine and into the 8 position of lepidine as a result of treatment of the ferricinium cation with the corresponding diazonium salts [72].

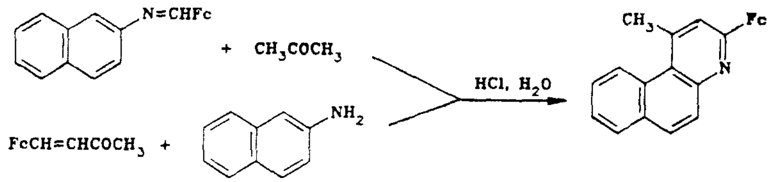
2-Quinolylferrocene derivatives were synthesized from 3-chloro-3-ferrocenylacroleine and substituted anilines. The reaction proceeds with the intermediate formation of immonium salts. It was established that of the two possible cyclization pathways, the one in which quinoline derivatives containing the Fc radical in the 2 position are obtained is realized [61]:



Ferrocenyl derivatives of quinoline and isoquinoline were synthesized in the reaction of quinoline or isoquinoline with phenylsulfonylbenzimidoyl chloride with subsequent treatment of the resulting salts with ferrocene [50]:



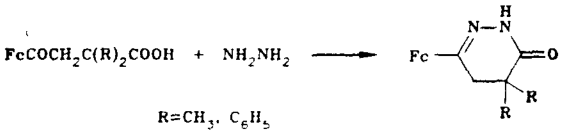
Two methods for obtaining 2-ferrocenyl-4-methylbenzo[f]quinoline have been proposed [73]:



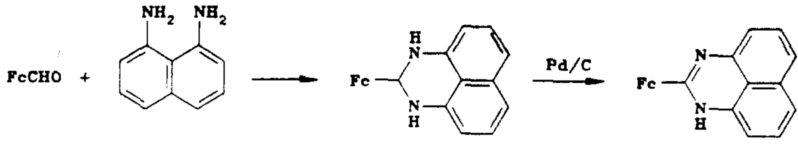
2-Pyridylferrocene and 2-quinolylferrocene, as well as their salts, are recommended as inhibitors of the corrosion of steel in acids—nonoxidizing agents [74].

2-Ferrocenyl-4-methyl-5,6-benzoquinoline methiodide has been patented as a dye for polyamide and polyester materials [75].

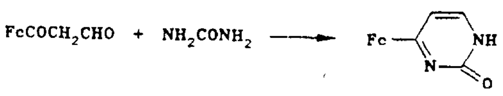
Cyclocondensation occurs in the reaction of γ-keto acids of the ferrocene series with hydrazine, and pyridazin-3-one derivatives are formed [76]:



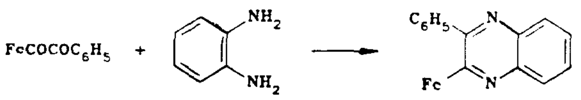
1-Ferrocenyl-2,3-dihydro-1H-permidine, which was converted to 1-ferrocenylperimidine by heating in xylene in the presence of Pd/C, was obtained by the reaction of formylferrocene with 1,8-diaminonaphthalene in the presence of p-toluenesulfonic acid [77]:



The condensation of ferrocenoylacetaldehyde with urea leads to the formation of 4-ferrocenylpyrimidin-2-one [28]:

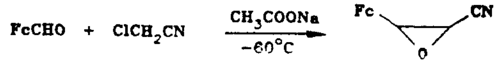


2-Ferrocenyl-3-phenylquinoxaline is formed in the condensation of ferrocenylphenylglyoxal with o-phenylenediamine [78]:

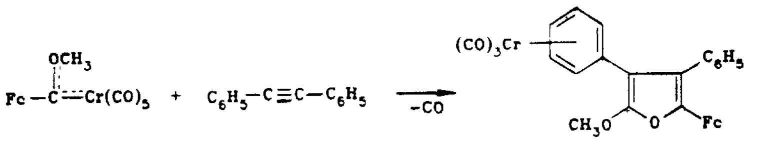


2. OXYGEN-CONTAINING HETARYLFERROCENES

There is a single report regarding the production of a ferrocene derivative containing an epoxide grouping [79]:

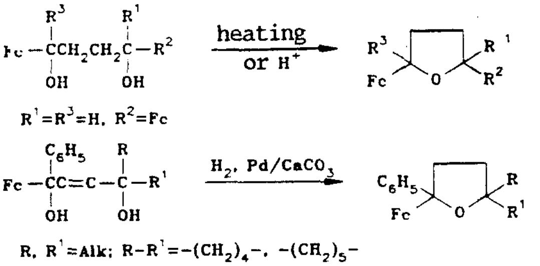


Tricarbonyl[(1-ferrocenyl-5-methoxy-3,4-diphenyl)furan]chromium was obtained from pentacarbonyl[ferrocenyl-(methoxy)carbene]chromium and tolan [80]:

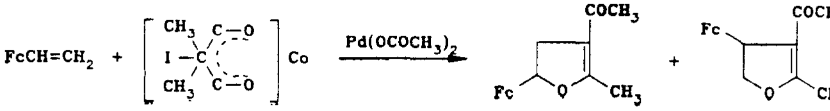


2-Ferrocenylbenzofuran is formed in the reaction of FcC≡CCu with o-iodophenol [81].

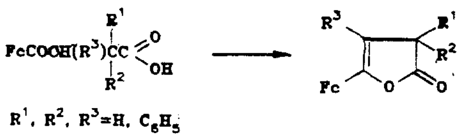
2-Ferrocenyltetrahydrofuran was synthesized by the reduction of $FcCOCH_2CH_2COOCH_3$ with lithium aluminum hydride [82]. Two methods have been developed for obtaining 2-ferrocenyltetrahydrofuran derivatives [83-86]:



A mixture of two ferrocenyldihydrofurans is formed in the reaction of vinylferrocene with cobalt tris(3-iodoacetylacetonate) in the presence of palladium diacetate [87]:

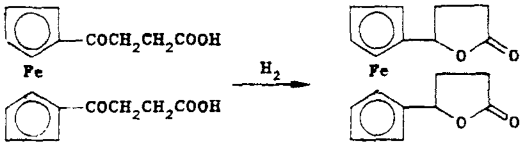


Substituted 4-ferrocenyl-4-oxobutyric acids undergo dehydration to give ferrocenylfuranone derivatives [78, 88]:



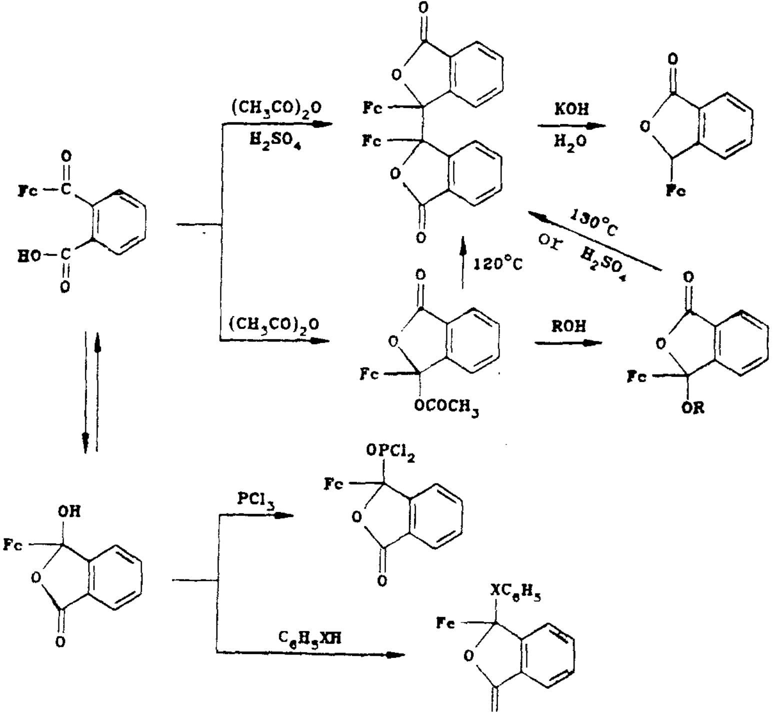
5-Ferrocenylbutyrolactone is formed as a result of treatment of β-ferrocenoylpropionic acid with sodium borohydride [1, 83].

The corresponding bislactone was obtained by catalytic hydrogenation of a ferrocene derivative containing two $-COCH_2CH_2COOH$ radicals [53]:



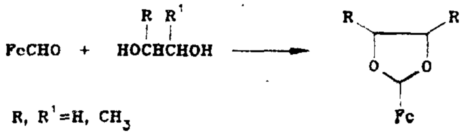
5,5-Diferrocenylbutyrolactone is formed as a result of the reaction of ferrocene with succinic acid chloride in the presence of aluminum chloride [83].

The reaction of o-carboxybenzoylferrocene with various reagents, which leads to phthalide derivatives, has been studied in quite some detail [89, 90]:

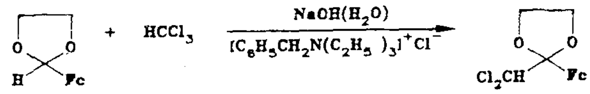


R=CH$_3$, C$_6$H$_5$; X=O, S

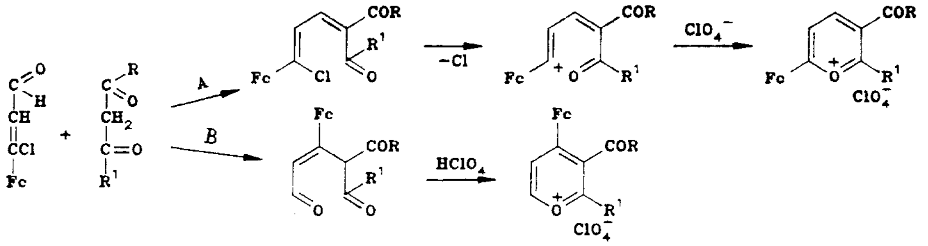
The acetalization of formylferrocene with the formation of 2-formyldioxolanes was accomplished by the action of α-glycols in the presence of p-toluenesulfonic acid [91, 92]:



Dichlorocarbene is incorporated into the C–H bond as a result of the treatment of 2-ferrocenyldioxolane with $HCCl_3$ and aqueous alkali under conditions of interphase catalysis [93]:



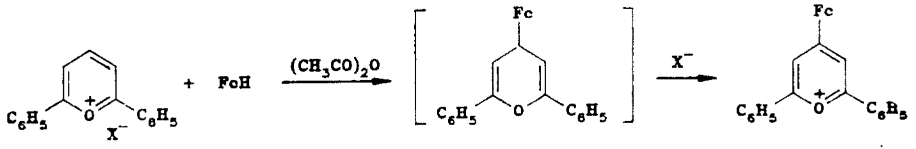
Depending on the reaction pathway, the formation of two types of compounds is possible in the reaction of 3-chloro-3-ferrocenylacrolein with 1,3-diketones:



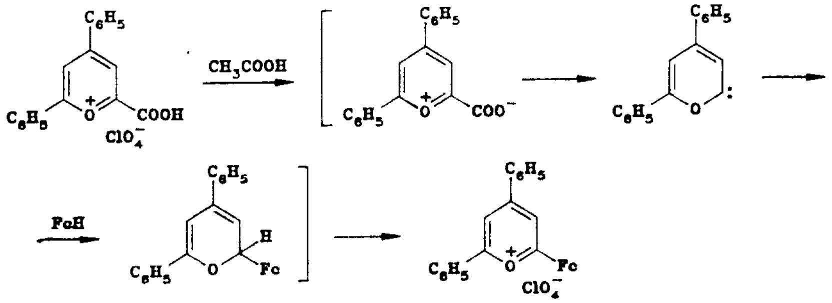
$R=R^1=C_6H_5$, CH_3; $R=C_2H_5O$, $R^1=CH_3$; $R-R^1=-CH_2C(CH_3)_2CH_2-$

Conversion of the pyrylium salts to pyridine bases and a study of their PMR spectra made it possible to establish that the reaction proceeds via pathway A [62].

Pyrylium salts that contain a ferrocenyl radical in the 4 position [60] or in the 2 position [59] were obtained by the direct pyrylation of ferrocene:



$X^-=HSO_4^-$, ClO_4^-, BF_4^-



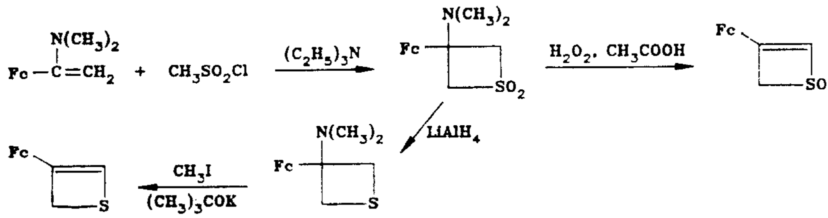
The last compound was also synthesized from acetylferrocene and chalcone [60].

Ferrocenyl o-carboxybenzyl ketone undergoes dehydration to give 2-ferrocenylisocoumarin [94].

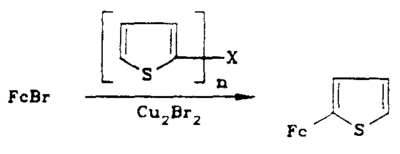
2-Ferrocenylchroman-4-one was synthesized by heating 2-ferrocenylvinyl o-hydroxyphenyl ketone in the presence of sodium acetate [95, 96]:

3. SULFUR-CONTAINING HETARYLFERROCENES

3-Ferrocenylthiete and its 1,1-dioxide were synthesized from 2-(dimethylamino)vinylferrocene and methanesulfonyl chloride [97]:

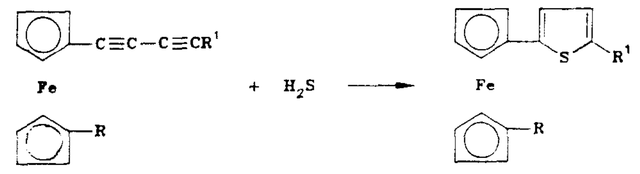


Nesmeyanov and co-workers [9, 10] obtained α-ferrocenylthiophene by the reaction of bromoferrocene with tetra(α-thienyl)boropotassium or with α-thienylmagnesium iodide in the presence of Cu_2Br_2 at 130°C:



X=BK, n=4; X=MgI, n=1

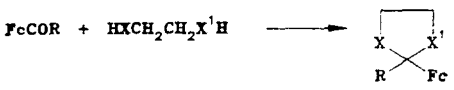
α-Ferrocenylthiophene derivatives are readily formed by treatment of the corresponding 1,4-disubstituted diacetylenes with hydrogen sulfide [98, 99]:



R=H, $R^1=CH_2OH$, C_6H_5, Fc; $R=CH_3$, $R^1=CH_2OH$, Ar

2-Hydroxymethyl-4-ferrocenylthiophene was oxidized with manganese(IV) oxide to the corresponding aldehyde and reduced with lithium aluminum hydride to 2-methyl-4-ferrocenylthiophene [98].

The corresponding oxathiolanes or dithiolanes were synthesized by the reaction of formylferrocene, acetylferrocene, or benzoylferrocene with β-hydroxy mercaptans or with dithioglycols in the presence of hydrogen chloride [92]:

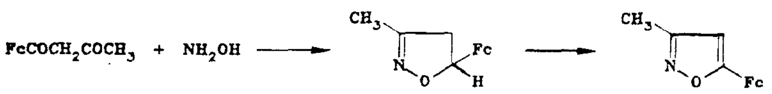


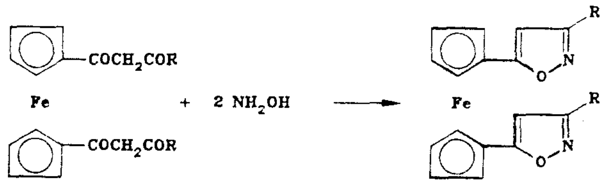
X=S, $X^1=O$; $X=X^1=S$; R=H, CH_3, C_6H_5

4. HETARYLFERROCENES CONTAINING SEVERAL DIFFERENT HETEROATOMS

According to the data in [30], two isomeric isoxazoles are formed in the reaction of ferrocenyl ethynyl ketone with hydroxylamine hydrochloride:

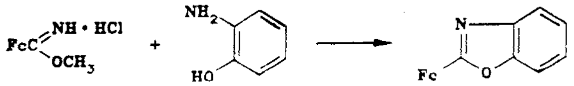
One isomer is formed in the reaction of hydroxylamine with 1,3-diketones $FcCOCH_2COR$ [24, 27]. Polyakov and co-workers explain this regioselectivity by the fact that the ferrocenyl radical displays greater electron-donor character (a greater +I effect) than the R radical:



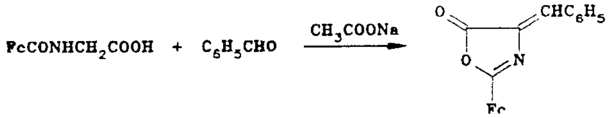


$R=CH_3$, $COOC_2H_5$

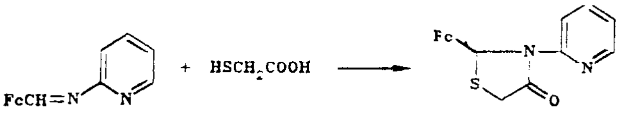
2-Ferrocenylbenzoxazole was obtained by condensation of methyl ferroceniminocarboxylate hydrochloride with o-aminophenol [49]:



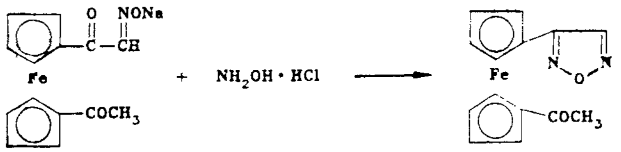
The condensation of N-ferrocenoylglycine with benzaldehyde in the presence of sodium acetate leads to 2-ferrocenyl-4-benzylideneoxazol-5-one [51]:



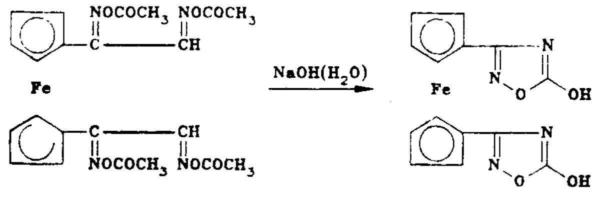
A thiazolone derivative is formed in the reaction of a ferrocenyl-containing azomethine with thioglycolic acid [8]:



Ferrocene derivatives that contain oxadiazole radicals were synthesized on the basis of 1,1'-diacylferrocene oximes. Thus, the expected 1,2,5-oxadiazole was obtained by treatment of the sodium salt of the monooxime with hydroxylamine hydrochloride [100]:

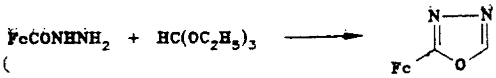


At the same time, when 1,1'-bis[1,2-(diacetoximino)ethyl]ferrocene is heated with aqueous alkali, cyclization leads not to the formation of a 1,2,5-oxadiazole derivative but rather to the formation of 1,1'-bis(5-hydroxy-1,2,4-oxadiazol-3-yl)ferrocene [100]:

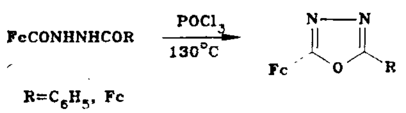


A transformation of this type is discussed in [101].

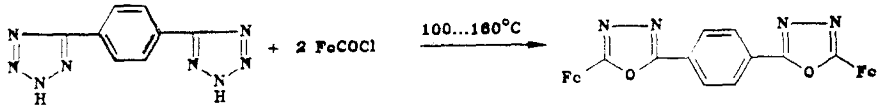
A widely known method for the synthesis of 1,3,4-oxadiazoles (by the action of an orthoformic ester on carboxylic acid hydrazides) was also used to obtain 2-ferrocenyl-1,3,4-oxadiazole [77]:

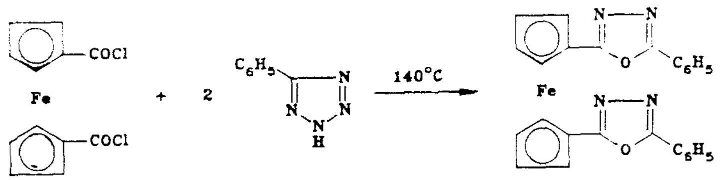


2,5-Diferrocenyl-1,3,4-oxadiazoles were also synthesized by a well-known method — by the reaction of N,N'-diacylhydrazines with phosphorus oxychloride [102]:



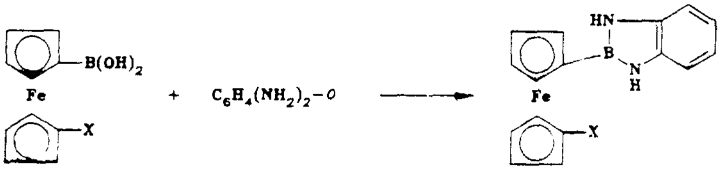
Compounds that contain two 1,3,4-oxadiazole fragments were similarly obtained [102]. Yet another method for the synthesis of ferrocenyl-1,3,4-oxadiazoles, which consists in heating tetrazole derivatives with ferrocenecarboxylic acid chlorides, has been described [102]:





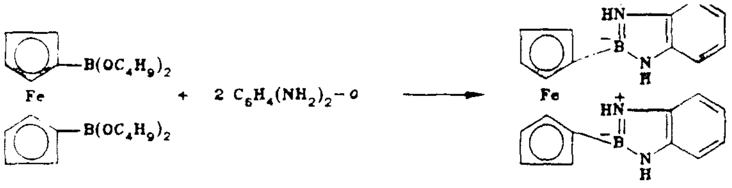
Poly(ferrocenyl-1,3,4-oxazoles) are formed in the case of treatment of polyhydrazides (FcCONHNHCO-RCONHNHCO)$_n$Fc with phosphorus oxychloride or by the reaction of 1,4-bis(5-tetrazolyl)benzene with 1,1'-ferrocenedicarboxylic acid dichloride [102].

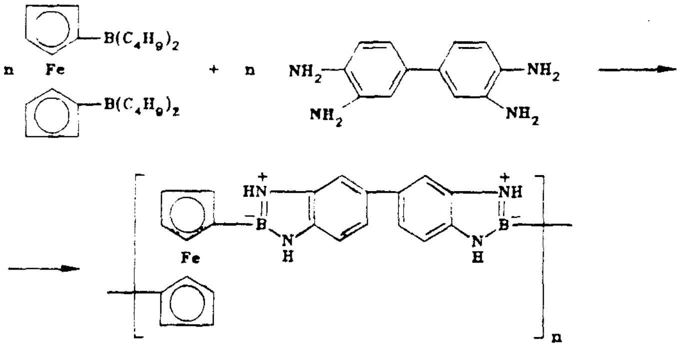
Nesmeyanov and co-workers obtained borabenzimidazolines by refluxing ferrocenylboric acids with o-phenylenediamine in toluene and assigned a structure to them [103]:



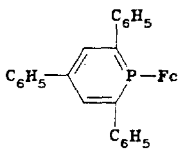
X=H, Cl, Br

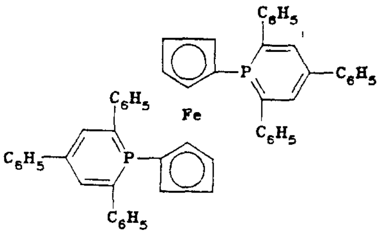
However, it was later established that compounds of this type exist in the form of bipolar ions [104]:





One should also note the synthesis of phosphorine derivatives that contain a ferrocenyl radical attached to the phosphorus atom. Such compounds are formed in the reaction of the mono- or dilithium derivative of ferrocene with 2,4,6-triphenylphosphorine [105]:





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SYNTHESIS OF 2-SUBSTITUTED 3-FORMYL-5-METHOXYTETRAHYDROFURANS FROM 2,5-DIMETHOXYTETRAHYDROFURYL-3-CARBINOLS

L. Yu. Brezhnev, M. M. Vartanyan, and A. V. Khandin

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The acid-catalyzed rearrangement of 2,5-dimethoxytetrahydrofuryl-3-carbinol, obtained from 2,5-dimethoxy-3-formyltetrahydrofuran, gave the 2-substituted 3-formyl-5-methoxytetrahydrofuran.

The purpose of our work was to study the properties of 2,5-dimethoxytetrahydrofuryl-3-carbinols (Ia-e), obtained from 3-formyl-2,5-dimethoxytetrahydrofuran (II) by hydrogenation with Raney nickel (Ia) [1], or by the Grignard reaction (Ib-e) (here and below all compounds were isolated as mixtures of syn- and anti-isomers, shown by the positions of the methoxy-group signals in the PMR spectra).

Alcohols Ia-e are 3-substituted cyclic diacetals and are sensitive to acid reagents. We have used this property to carry out the acid-catalyzed rearrangement of the alcohols.

Earlier, it was shown that 2-hydroxymethyl-2,5-dimethoxytetrahydrofuran was converted to 4-methoxy-2,7-dioxabicyclo[2.2.1]pentane [2] by an acid ion-exchange resin. We found that when the alcohols Ia-e were refluxed in acetic acid they underwent rearrangement to 2-substituted 3-formyl-5-methoxytetrahydrofurans (IIIa-e, Table 1).

We propose that the mechanism of the reaction is that of intramolecular acetalization.

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 164-166, February, 1991. Original article submitted June 27, 1989.