

Data on methods of synthesis, transformations, and spectroscopy of monocyclic six-membered, oxygen-containing heterocycles, viz., 2H-pyrans, are correlated and systematized for the first time in this review.

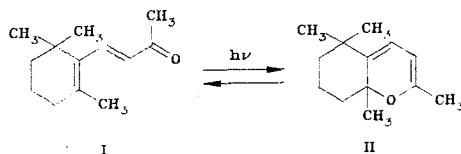
INTRODUCTION

Correlated information regarding the synthesis and properties of 2H-pyrans is not available in the literature dealing with the chemistry of heterocyclic compounds [1].* This situation is not by chance, since unsubstituted 2H-pyran was unknown until recently, and reliable data on the synthesis of derivatives of this heterocycle did not appear until 1957 [3]. The principal reason for the inaccessibility of α -pyrans and their derivatives consists in their low stability, which is associated with their conversion to valence isomers, viz., cis-dienones, under tautomeric equilibrium conditions [4, 5]. In addition to this, methods for the synthesis of derivatives of 2H-pyrans have been developed over the last 25 years, definite progress has been made in the study of the valence isomerism of this class of heterocycles, and their physical properties and chemical transformations have been studied.

The present review is devoted to the correlation and systematization of these data.

1. Synthesis and Valence Isomerism of 2H-Pyrans

The simplest unsubstituted 2H-pyran was not obtained until recently. The synthesis of methyl-2H-pyran was reported in 1917 [6]; however, in 1921 von Auwers showed that this compound is 2-vinyl-2,5-dihydrofuran. A relatively simple α -pyran (II) was first isolated in 1957 by irradiation of trans- β -ionone (I) [3]:

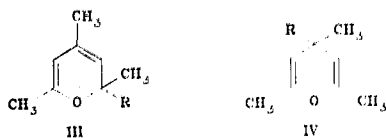


There are currently four principal methods for the preparation of 2H-pyrans in which pyrylium salts, unsaturated acyclic ketones, 4H-pyrans, and α -pyrones are used as the starting substances.

1.1. Synthesis on the Basis of Pyrylium Salts. One of the principal methods for the preparation of 2H-pyrans is the reaction of pyrylium salts with organometallic compounds [8-19]; in addition to 2H-pyrans, their cis-dienone valence isomers, as well as 4H-pyrans, are formed in this case. The ratio of the substances obtained is determined by the structure of the pyrylium salt, the nature of the nucleophilic reagent, and the reaction conditions [19].

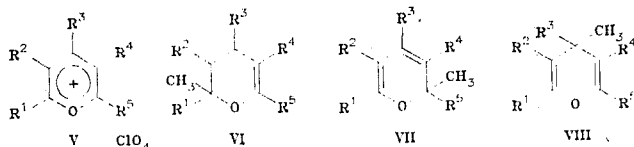
Thus the reaction of 2,4,6-trimethylpyrylium perchlorate with various alkylmagnesium halides was studied [16]. Data on the ratios of the resulting 2H- (III) and 4H-pyrans (IV) are presented in Table 1. The compositions of the products of the given reactions (in molar percent) were determined in the gas phase.

*A review of methods of synthesis and the properties of 4H-pyrans was published in 1983 [2].



III, IV a R=CH₃, b R=C₂H₅, c R=*n*-C₃H₇, d R=*n*-C₄H₉, e R=*i*-C₄H₉, f R=*i*-C₃H₇,
g R=*s*-C₄H₉, h R=*t*-C₄H₉

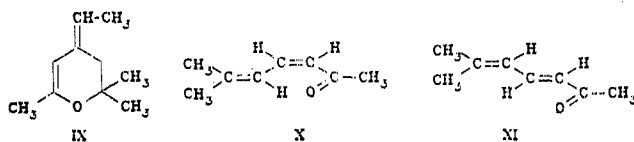
The reaction of a series of pyrylium perchlorates V (Table 2) with methylmagnesium iodide was examined in [17] in order to ascertain the effect of substituents in the pyrylium cation on the orientation of attack by the nucleophile. The effect of substituents in the 2 and 6 positions of 2,6-dialkyl-4-methylpyrylium salts with either identical (Va-d) or different (Ve-h) substituents, of a methyl group in the 3 position in the case of 2,3,4,6-tetramethylpyrylium perchlorate (Vi), and of substituents in the 4 position of pyrylium salts with methyl groups in the 2 and 6 positions (Vj-m) was studied successively.



2H-Pyrans VIIIa, b, respectively, were obtained with 2,4,6-trimethylpyrylium perchlorate (Va) and 2,6-diethyl-4-methylpyrylium perchlorate (Vb). On the other hand, in addition to 2H-pyrans VIc, e, 4H-pyrans VIIIc-e are formed with 4-methyl-di-*n*-propylpyrylium (Vc), 2,6-di-*n*-butyl-4-methylpyrylium (Vd), and 4-methyl-2,6-di-*tert*-butylpyrylium perchlorates; the yields of 4H-pyrans VIIIc-e increase with an increase in the molecular mass of the substituents in the 2 and 6 positions. However, methylmagnesium iodide does not react with 4-methyl-2,6-diphenylpyrylium perchlorate (Vf) under these conditions. Methylmagnesium iodide reacts with 2-ethyl-4,6-dimethylpyrylium perchlorate (Vg) to give a mixture of 2-ethyl-2,4,6-trimethyl-2H-pyran (VIg) (65%) and 6-ethyl-2,2,4-trimethyl-2H-pyran (VIIg) (35%), which could not be separated. 4,6-Dimethyl-2-phenylpyrylium perchlorate (Vh) is attacked by methylmagnesium iodide exclusively in the 6 position to give 2,2,4-trimethyl-6-phenyl-2H-pyran (VIIh), an extremely unstable compound that cannot be purified by distillation. The condensation of methylmagnesium iodide with a mixture of pyrylium salts Vi (84%) and Vj (16%) leads to 2H-pyrans VIIi (90%) and VIj (9%).

Methylmagnesium iodide reacts with 4-ethyl-2,6-dimethylpyrylium perchlorate (Vj) to give 4-ethyl-2,4,6-trimethyl-2H-pyran (VIj); the latter undergoes complete isomerization under the influence of traces of acid to give 4-ethylidene-2,2,6-trimethyl-3,4-dihydro-2H-pyran (IX). 2,2,6-Trimethyl-4-phenyl-2H-pyran (VIk) is obtained when 2,6-dimethyl-4-phenylpyrylium perchlorate (Vk) is treated with methylmagnesium iodide.

The action of methylmagnesium iodide on 2,6-dimethylpyrylium perchlorate (Vl) leads to a mixture of 2H-pyran VIIl (45%), 6-methyl-3,5-heptadien-2-one (X) (25%), and 6-methyl-3,5-heptadien-2-one (XI) (25%).



2H-Pyran VIIl, which is formed in small amounts, is extremely unstable.

The action of methylmagnesium iodide on 2,6-dimethylpyrylium perchlorate (Vl) was compared with the action of the same reagent on 2,3,5,6-tetramethylpyrylium perchlorate (Vm) in order to study the effect of substituents in the 3 and 5 positions on the orientation of nucleophilic attack. The reaction with Vm leads to a mixture of 2H-pyran VIIl (48%) and 4H-pyran VIIIl (52%). The percentages of the products of attack by methylmagnesium iodide at the α and γ positions of pyrylium salts Vl and Vm are identical, and it may therefore be concluded that the substituents in the 3 and 5 positions do not affect the yields of the reaction.

A theoretical study of the reaction of pyrylium salts with alkylmagnesium halides has been accomplished by means of quantum-chemical methods [15, 18], as well as by means of the theory of hard and soft acids and bases [18]. However, clear-cut conclusions were not drawn, since the methods used had substantial limitations.

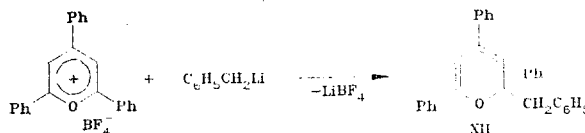
TABLE 1. Ratios of the 2H- (III) and 4H-Pyrans (IV) Obtained in the Reaction of Alkylmagnesium Halides with 2,4,6-Trimethylpyrylium Perchlorate

| Com- pound | x in RMgX | a | b | c | d | e | f | g | h |
|---------------|--------------|-----|----|----|----|----|-----|-----|----|
| III | I | 100 | 52 | 52 | 46 | 51 | 0 | 0 | 52 |
| IV | I | 0 | 48 | 48 | 54 | 49 | 100 | 100 | 48 |
| III | Br | — | 60 | 57 | 50 | 50 | 0 | 0 | 57 |
| IV | Br | — | 40 | 43 | 50 | 40 | 100 | 100 | 43 |
| III | Cl | — | — | 43 | 45 | 46 | 0 | 0 | 50 |
| IV | Cl | — | — | 57 | 55 | 54 | 100 | 100 | 50 |

TABLE 2. Pyrylium Perchlorates V Investigated in Their Reaction with Methylmagnesium Iodide

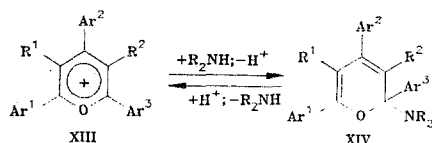
| Com- pound | R ¹ | R ² | R ³ | R ⁴ | R ⁵ |
|---------------|---|-----------------|-------------------------------|-----------------|---|
| Va | CH ₃ | H | CH ₃ | H | CH ₃ |
| Vb | C ₂ H ₅ | H | CH ₃ | H | C ₂ H ₅ |
| Vc | <i>n</i> -C ₃ H ₇ | H | CH ₃ | H | <i>n</i> -C ₃ H ₇ |
| Vd | <i>n</i> -C ₄ H ₉ | H | CH ₃ | H | <i>n</i> -C ₄ H ₉ |
| Ve | <i>t</i> -C ₄ H ₉ | H | CH ₃ | H | C ₆ H ₅ |
| Vf | C ₆ H ₅ | H | CH ₃ | H | CH ₃ |
| Vg | C ₆ H ₅ | H | CH ₃ | H | CH ₃ |
| Vh | CH ₃ | H | CH ₃ | H | CH ₃ |
| Vi | CH ₃ | CH ₃ | CH ₃ | H | CH ₃ |
| Vj | CH ₃ | H | C ₂ H ₅ | H | CH ₃ |
| Vk | CH ₃ | H | C ₂ H ₅ | H | CH ₃ |
| VI | CH ₃ | H | H | H | CH ₃ |
| Vm | CH ₃ | CH ₃ | H | CH ₃ | CH ₃ |

2H-Pyran XII was isolated in 35% yield in the reaction of benzyllithium with 2,4,6-triphenylpyrylium tetrafluoroborate [8]:



4-Methyl-6-phenylhepta-3,5-dien-2-one — a valence tautomer of the corresponding 2H-pyran — was obtained in high yield by the action of phenylmagnesium bromide or phenyllithium on 2,4,6-trimethylpyrylium perchlorate [10-12]. Similarly, the open form of the corresponding pyran — 1,2,3,4,5,6-hexaphenylhepta-3,5-dien-2-one — is formed from the pentaphenylpyrylium salt and benzylmagnesium chloride [9].*

In [20] it was shown that by the action of dialkylamines in aprotic solvents (for example, diethyl ether) on pyrylium salts XIII one can isolate, in crystalline form, stable 2H-pyran derivatives XIV, the structures of which were proved by ¹³C and ¹H NMR spectroscopy and by UV spectroscopy.



Fischer and co-workers [20] explain the possibility of the isolation of stable 2H-pyrans by the presence of substituents in the 3 position or 3 and 5 positions of the pyrylium ring.

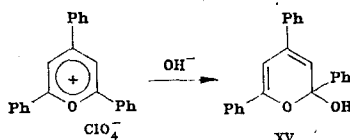
Complex metal hydrides (NaBH₄, LiBH₄, KBH₄) react with pyrylium salts to give unstable 2-monosubstituted 2H-pyrans [21-26], which undergo rapid isomerization to the corresponding cis-dienones.

*2,4,6-Trisubstituted pyrylium salts react with benzylmagnesium chloride (in contrast to other alkyl- and arylmagnesium halides) to give exclusively 4H-pyrans; 2,3,4,6-tetrasubstituted pyrylium salts also react similarly [9].

In [23] it was shown that the reaction of sodium borohydride or, better yet, lithium borohydride with 2,3,4,5,6-pentaphenylpyrylium salt at a low temperature (-70°C) leads to the formation of the corresponding 2H- (66%) and 4H-pyran (10%). However, the latter could not be isolated in crystalline form, since it undergoes quantitative isomerization to the cis-dienone at elevated temperatures.

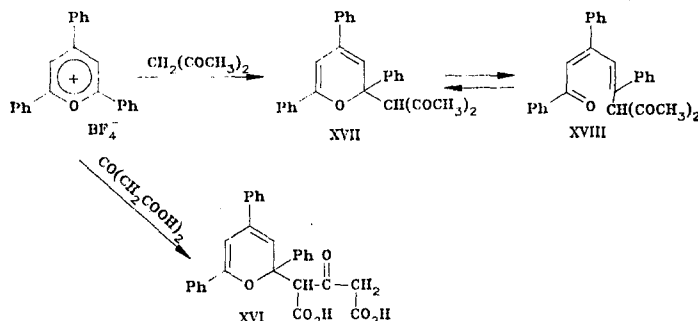
It is characteristic that in all cases the reaction of complex metal hydrides with pyrylium salts leads to the formation of, in addition to the valence isomers of 2H-pyrans, viz., cis-dienones, the corresponding 4H-pyrans or their open forms, viz., saturated 1,5-diketones [23-26].

The products of hydrolysis and alcoholysis of pyrylium salts [27-33] can also be regarded as hydroxy and alkoxy derivatives of 2H-pyrans. These cyclic compounds are unstable and require special conditions for isolation. Thus the corresponding α -pyranol XV can be isolated in the hydrolysis of 2,4,6-triphenylpyrylium perchlorate in a strongly alkaline medium (pH 14) with the use of a buffer methanol solution [27]:



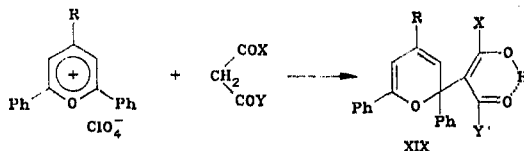
Since the formation of noncyclic compounds such as pentenediones and keto enols is also possible during alcoholysis or hydrolysis, spectral methods are widely used for identification. Thus Katritzky and co-workers [33] demonstrated by means of ^{13}C NMR spectroscopy that alkoxy-2H-pyrans are formed in the reaction of a number of pyrylium salts with the methoxide anion.

Upon reaction with CH-acid compounds pyrylium salts are also capable of forming 2H-pyran derivatives. For example, 2,4,6-triphenylpyrylium tetrafluoroborate reacts with acetonedicarboxylic acid to give 2H-pyran XVI [34]:



The same pyrylium salt reacts with acetylacetone to give a substance, the structure of which was not accurately established; one of the hypothetical forms is XVIII, which is the open form of the corresponding 2H-pyran XVII [34].

Interphase catalysis offers a significantly greater possibility for the synthesis of 2H-pyrans with the participation of CH-acid compounds [35]. Thus the reaction of 2,4,6-triphenyl- and 2,6-diphenyl-4-(α -thienyl)pyrylium perchlorates with acetoacetic ester, acetyl acetate, and malonic ester leads to 2H-pyrans XIX:

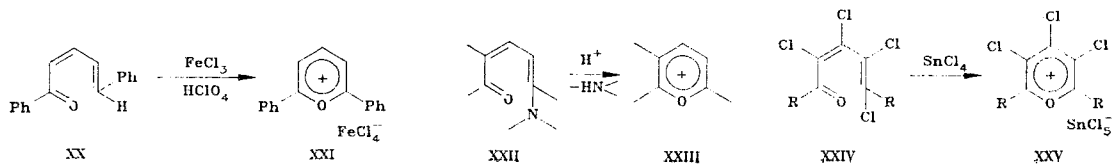


a-c R=Ph, d R= α -thienyl; a, b X=Me, c, d X=OEt; a, c, d Y=OEt, b Y=Me

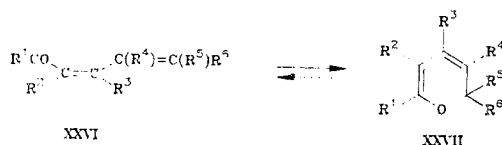
The reactions are carried out by stirring an ether suspension of the pyrylium salt with the methylene-active compound, an alkaline agent (30% NaOH or solid Na_2CO_3), and a catalyst, viz., triethylbenzylammonium chloride, at room temperature. Compounds XIXc, d are isolated from the reaction mixture in the form of the sodium enolates, and acidification of the latter leads to the free 2H-pyrans.

It is customary to postulate the development of 2H-pyrans as the first step in the reaction of pyrylium salts with various nucleophiles, which then leads either to recyclization products [36, 37] or to ring-opening products [38, 39].

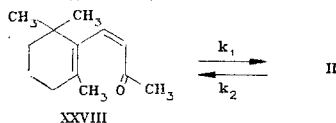
It should be noted that reconversion to pyrylium salts is not characteristic for 2H-pyrans. However, in the presence of acidic reagents dienone derivatives (valence tautomers of 2H-pyrans) XX, XXII, and XXIV undergo cyclization to give pyrylium cations XXI, XXIII, and XXV [40-43]. Starting compounds XX, XXII, and XXIV can be obtained by specific methods such as the preparation of cinnamylideneacetophenone (XX) by the method in [44].



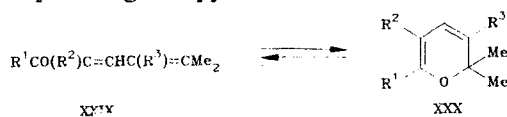
1.2. Synthesis of 2H-Pyrans by Cyclization of Unsaturated Ketones. Valence Tautomerism of 2H-Pyrans. The phenomenon of valence isomerism is characteristic for 2H-pyrans [45]: one observes a symmetry-permitted, thermal pericyclic process [46, 47] that has a low energy of activation. As a result, one observes a fast and reversible equilibrium between the valence tautomers: cis-dienones XXVI and 2H-pyrans XXVII [48-69]. This can be regarded as a method for the preparation of the latter.



The study of the valence isomerization is carried out very conveniently by means of NMR spectroscopy. Thus Marvell and co-workers [51] first studied valence isomerization in the equilibrium system cis- β -ionone (XXVIII) \rightleftharpoons 1-oxa-2,5,5,9-tetramethyl-1,5,6,7,8,19-hexahydro-naphthalene (II) by PMR spectroscopy.



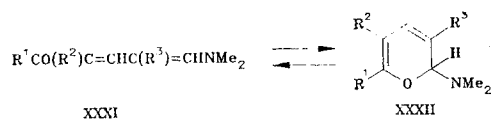
The PMR method was also used in [65] to study the valence isomerization of compounds of the XXIX type, which leads to the establishment of a dynamic equilibrium between 1,1-dicarbonyl 1,3-dienes and the corresponding 2H-pyrans XXX:



XXIX, XXX $R^1 = \text{Me, Ph}$; $R^2 = \text{MeO}_2\text{C, MeCO}$; $R^3 = \text{H, Me}$

Moreover, the ^{13}C NMR spectra of these compounds have been studied [67]. The relatively high energy barrier of valence isomerization, the magnitude of which for $\Delta G_{303^\circ\text{K}}$ in the investigated series of compounds in CDCl_3 , CD_3CN , $\text{CD}_3\text{OD} \geq 21.7$ kcal/mole, made it possible, when appreciable amounts of both isomers were present in the equilibrium mixture, to observe two sets of lines in the NMR spectra. The effect of structural factors and solvents on the position of the equilibrium was established as a result of a direct study of the valence isomerization, and the thermodynamic and activation parameters of the valence isomerization of XXIX and XXX were also determined.

It has been shown by means of ^1H and ^{13}C NMR spectra that a dynamic equilibrium between 1-carbonyl-3-methyl(phenyl)-4-dimethylamino 1,3-diketones XXXI and the corresponding 2H-pyrans XXXII is established as a result of valence isomerization [68]:



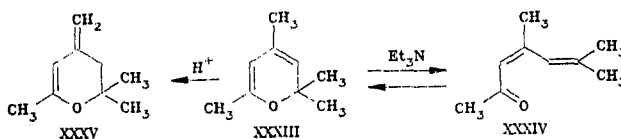
The position of the dienone \rightleftharpoons 2H-pyran equilibrium depends on the solvent. The equilibrium is shifted to favor δ -amino dienones as the dielectric constant of the solvent and its capacity for specific solvation increase.

Thus in CDCl_3 , CD_3CN , and absolute CD_3OD , as well as without a solvent, the equilibrium is shifted significantly to favor the 2H-pyran, whereas in D_2O it is shifted to favor the acyclic dienone form. The position of the equilibrium has an intermediate value in aqueous methanol solutions.

The free energies of activation of the valence isomerization of XXXI and XXXII in aqueous methanol solutions have been estimated. The value of the rate constants of this process for the indicated pairs of valence isomers is greater by a factor of at least 10^8 than for compounds of the XXIX \rightleftharpoons XXX type.

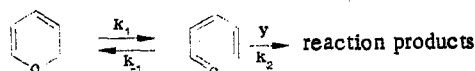
The aggregate state can affect the existence of δ -aminodienones in one or another isomeric form. Thus XXXI ($\text{R}^1 = \text{R}^2 = \text{Me}$, $\text{R}^3 = \text{COOMe}$) in the crystalline state is a dienone, whereas in the fused state it exists in the form of 2H-pyran XXXII [66].

Tautomeric equilibrium of the type under consideration has also been studied for 2,2,4,6-tetramethyl- α -pyran (XXXIII) [51]. In an attempt to determine the amount of isomeric dienone XXXIV by NMR spectroscopy in CCl_4 , 2H-pyran XXXIII was converted to 2,2,6-trimethyl-4-methylene-3,4-dihydro-2H-pyran (XXXV).



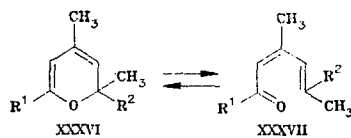
Proton migration is not observed in anhydrous pyridine; moreover, the electrocyclic process also is not followed clearly. In triethylamine, however, one observes peaks that can be ascribed to dienone XXXIV, and their intensities increase as the temperature is increased; nevertheless, the amount of 2H-pyran XXXIII that exists in equilibrium is insufficient for quantitative measurements.

Huisgen [70, 71] has proposed the utilization of the bimolecular reaction of the less stable compound of a pair of valence isomers to measure the rate of conversion of the more stable isomer to the less stable isomer. In the case under consideration, where Y is the selective reagent that reacts with the dienone, the scheme has the form



Organometallic compounds were selected as reagent Y. The utilization of lithium aluminum hydride proved to be the most convenient course.

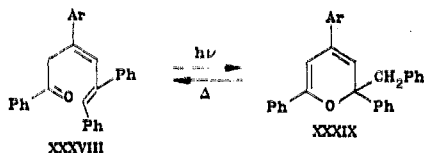
The kinetics of this process for isomers II and XXVIII and XXXVI and XXXVII were studied by this method, and the rate constants of these reactions were determined [5].



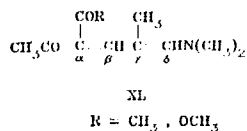
XXXVI, XXXVII a $\text{R}^1 = \text{R}^2 = \text{Me}$, b $\text{R}^1 = \text{R}^2 = \text{Ph}$

Quantum-chemical calculation (*ab initio*) with the 4-31G orbitals as the basis [72] indicates the relative instability of the cyclic isomer.

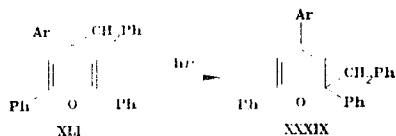
Under the influence of irradiation unsaturated ketones such as 4,6-dimethyl- and 5-methyl-3,5-heptadienone undergo cyclization to give the corresponding 2H-pyrans [73]. Similar cyclization to 2H-pyrans XXXIX is also characteristic for unconjugated dienes XXXVIII [74]:



These transformations can be regarded as one of the methods for the preparation of 2H-pyrans. It has also been reported [75] that in the case of δ -amino carbonyl compounds XL cyclization of the cis isomer relative to the γ , δ bond of the dienone with $R = OCH_3$ occurs. However, data that provide evidence that in the case of XL only photochemical cis-trans isomerization about the $C_\alpha=C_\beta$ bond, rather than photochemical cyclization to 2H-pyrans, takes place are presented in [76].

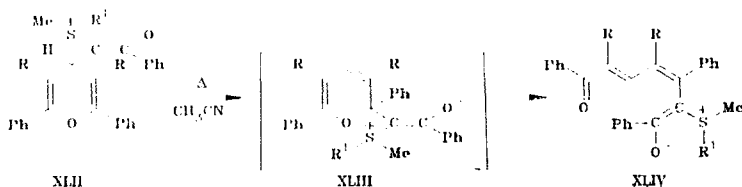


1.3. Synthesis of 2H-Pyrans by Isomerization of 4H-Pyrans. The corresponding 2H-pyrans XXXIX are readily formed under the influence of irradiation on 4H-pyrans XLI, which contain a benzyl group in the γ position [9, 74, 77, 78]:



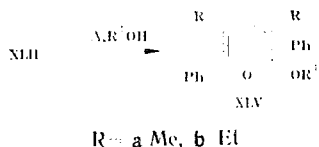
The migration of the benzyl group in the photoisomerization of 4H-pyrans XLI takes place via a singlet mechanism. Evidence regarding the position of the double bonds and the substituting groups in the isomeric heteroring is provided by its ability to react with maleic anhydride, to form a transannular peroxide in the case of sensitized photooxidation, etc. (see Sec. 2.3).

4H-Pyrans XLII, which contain an ylide grouping in the 4 position, during thermal rearrangement form open forms XLIII, which exist as two geometrical isomers [79]. There is no doubt that the first step in the indicated rearrangement is the formation of 2H-pyran XLIII, which then undergoes valence isomerization to the corresponding dienones:

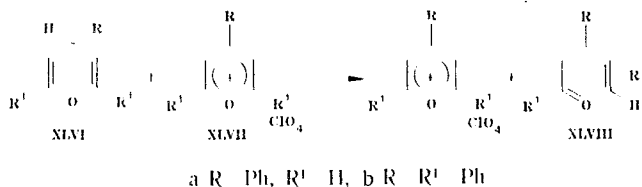


Similar opening of the pyran ring is also observed in the rearrangement of 2,4,6-triphenyl-4H-pyran in acetic acid [80].

Alkoxy-2H-pyrans XLV are formed in the thermal rearrangement of 4H-pyrans XLII, which contain a sulfonyl ylide grouping in the γ position, in methanol or ethanol [79]:

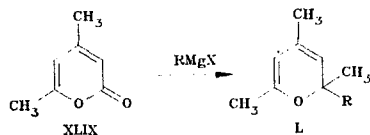


The hydride lability of 4H-pyrans with respect to 2H-pyran and its open-chain isomer, viz., the dienone, was studied in [81]; pyrylium cations were used as hydride-ion acceptors. Treatment of 2,6-diphenyl- (XLVIa) and 2,4,6-triphenyl-4H-pyran (XLVIb) with the corresponding pyrylium cations XLVII leads to the formation of cinnamylideneacetophenone (XLVIIIa) and 1,3,5-triphenylpenta-2,4-dienone (XLVIIIb), respectively:



Thus it was demonstrated that the product formed in the course of hydride transfer from the 4H-pyran to the 2 position of the pyrylium ring is a 2H-pyran, which undergoes valence isomerization to give the more stable open form. In other words, 4H-pyrans are less stable than 2H-pyrans, which, in turn, are less stable than their cis-dienone isomers.

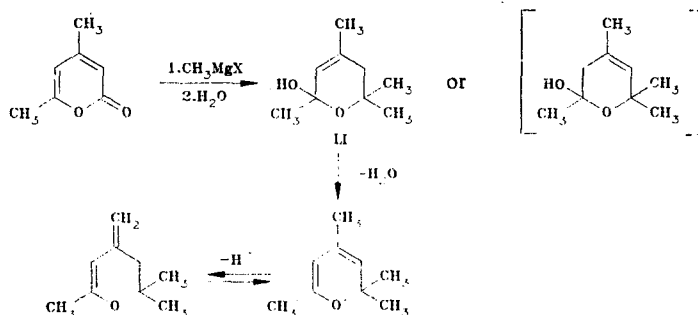
1.4. Preparation of 2H-Pyrans from α -Pyrone. The action of Grignard reagents on α -pyrones is one of the principal methods for the preparation of 2H-pyrans. Gompper and Christmann first reported [82, 83] the preparation of 2H-pyrans L by the action of organomagnesium compounds on 2,4-dimethyl- α -pyrone (XLIX):



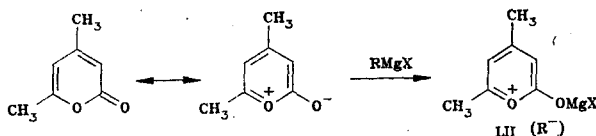
In repeating this synthesis Dreux and co-workers [84-89] established that the products of the reaction of pyrone XLIX with methylmagnesium iodide contained two isomers, viz., XXXIII and XXXV.

The isolation from the products of ketolization of acetone of a fraction with bp 145-150°C, which contained these two isomers, viz., 2,2,4,6-tetramethyl-2H-pyran (XXXIII) and 2,2,6-trimethyl-4-methylene-3,4-dihydro-2H-pyran (XXXV), served as the impetus for the study of these reactions. It was demonstrated by gas-liquid chromatography (GLC) that the isomers exist in equal ratios, and the isomers were separated by the same method [84-88].

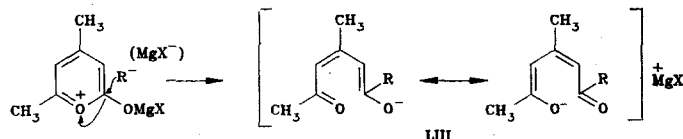
The isolation of the rather unstable 6-hydroxy-2,2,4,6-tetramethyl-3,6-dihydro-2H-pyran (LI) as an intermediate in the reaction of 2,4-dimethyl- α -pyrone with methylmagnesium iodide made it possible to propose the following reaction mechanism [89]:



It is characteristic that in the formation of 2H-pyrans via the reaction of α -pyrones with Grignard reagents one must use a threefold excess of the latter as compared with the stoichiometrically required amount. On the basis of experimental data it has been shown [89] that a complex of the pyrone with the Grignard reagent with a structure of the LII type* is initially formed:

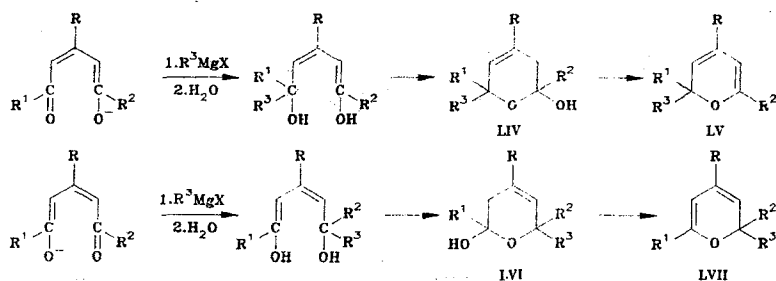


During the action of a second molecule of the alkylmagnesium halide the ring opens to give enolate ion LIII, which exists in two isomeric forms (which are identical when R = CH₃):



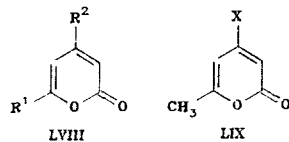
Finally, the enolate ion undergoes attack by a third molecule of the organomagnesium compound, and this leads to two different 2H-pyrans LV and LVII:

*The complex is a colored compound that during hydrolysis, which proceeds slowly even in an acidic medium, undergoes decomposition with liberation of the starting α -pyrone.



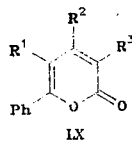
It is characteristic that dihydropyrans LIV and LVIII can be isolated only in the case of hydrolysis in a neutral medium. α -Pyrans LV and LVII are isolated in the case of acidic hydrolysis [89-91].

The products of the reaction of α -pyrones LVIII and LIX with alkylmagnesium halides are 2H-pyrans, as well as noncyclic compounds: diethylene aldehydes and ketones, as well as saturated 1,5-diketones [92].



LVIII a $R^1=R^2=H$; b $R^1=H$, $R^2=Me$; c $R^1=Me$, $R^2=Et$; LIX a $X=OH$; b $X=Cl$; c $X=OMe$

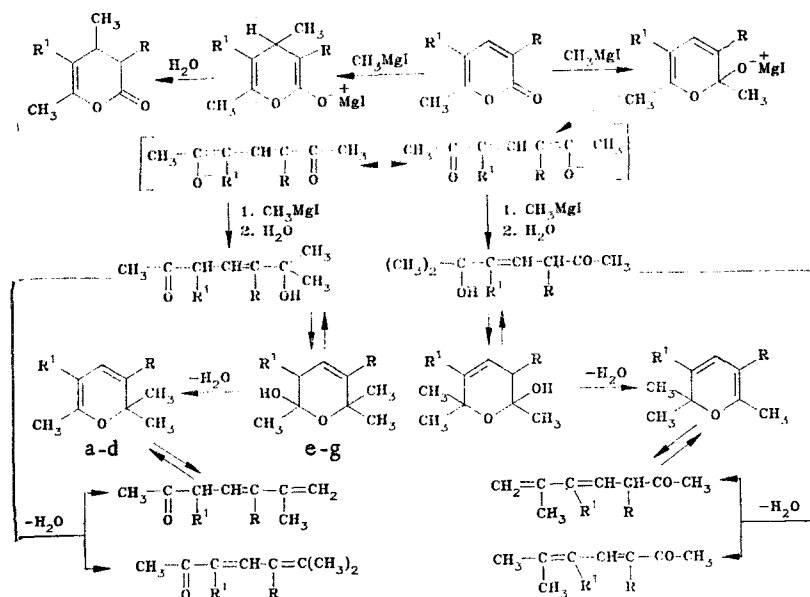
The reaction of alkylmagnesium halides with α -pyrones LX, which contain a phenyl group in the 6 position was studied in [93].



a, c-e $R^1=R^2=H$; b $R^1=Me$; a $R^3=H$; b $R^2=R^3=H$; c, d $R^3=Me$; e $R^3=Ph$

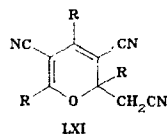
Depending on the structure of starting pyrone LX, keto enols, diethylene ketones, saturated 1,5-diketones, and dihydropyrans can be detected among the products of the reaction with Grignard reagents.

A study of the reaction of methylmagnesium iodide with 4-unsubstituted α -pyrones showed [94-95] that 2H-pyrans can be obtained only in the case of 3,5,6-trisubstituted α -pyrones. 5,6-Disubstituted α -pyrones give exclusively compounds that have linear structures (ketols, dienones):

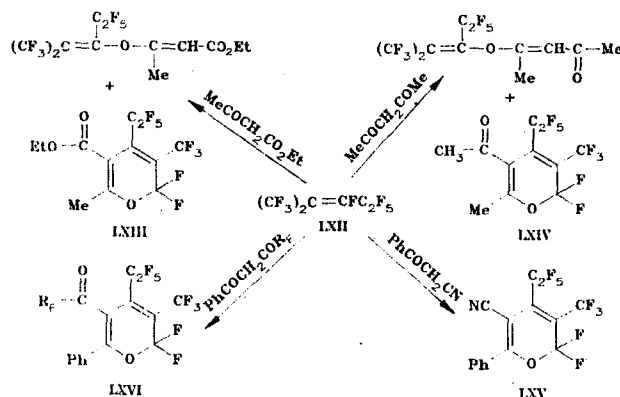


a, d $R=CH_3$, b, f $R=C_6H_5$; c, e $R=H$, g $R=R^1=H$; a-d $R^1=CH_3$, e $R^1=i-C_3H_7$, f $R^1=H$

1.5. Condensation Reactions. The synthesis of 2H-pyrans via condensation reactions has recently become realizable [96-98]. Thus cyano-substituted 2H-pyran derivatives LXIV were obtained in the thermal condensation of the corresponding aroylacetonitriles RCOCH₂CN [96, 97]. The exceptional stability of these pyrans was attributed to the presence of a cyano group.



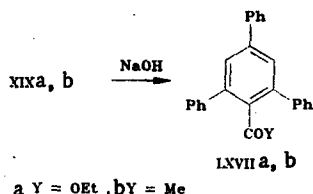
Fluorinated 2H-pyrans LXIII-LXVI were isolated as a result of the condensation of perfluoro-2-methyl-2-pentene (LXII) in acetonitrile in the presence of potassium fluoride [98]:



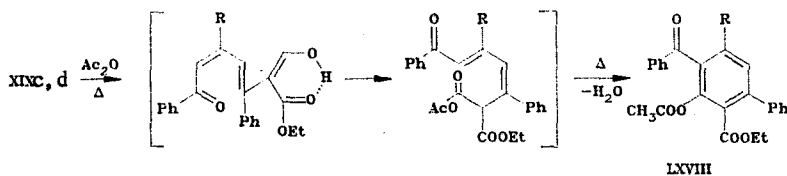
2. Transformations of 2H-Pyrans

2.1. Recyclization to Aromatic Compounds. The reaction of 2H-pyrans XIV with CH-acid compounds, nitromethane, and cyanoacetic ester leads to benzene derivatives [20].

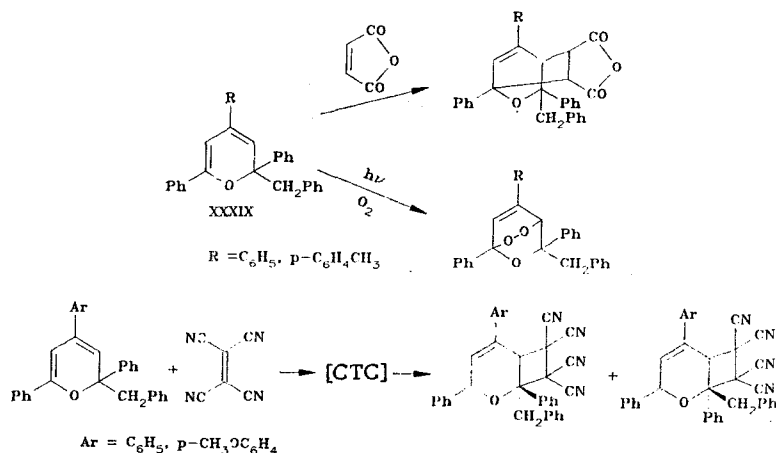
2,2-Disubstituted 2H-pyrans XIXa, b are converted to aromatic derivatives LXVII under the influence of an aqueous alcohol solution of sodium hydroxide [34]. Derivatives LXVII were also obtained by the reaction of pyrylium salts with CH acid compounds in the presence of potassium tert-butoxide [8], and this serves as weighty evidence that confirms the assumption of the intermediate formation of 2H-pyrans in the reactions of pyrylium salts with nucleophilic agents and, in particular, methylene-active compounds.



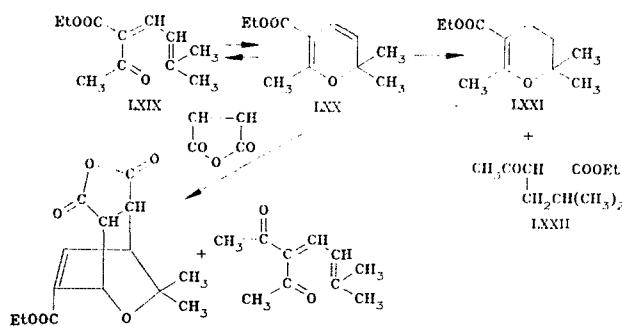
When 2H-pyrans XIXc, d are refluxed in acetic anhydride, recyclization proceeds via a different pathway and leads to the formation of acetylsalicylic acid derivatives LXVIII [34], which are extremely difficult to obtain by other methods.



2.2. Reactions with the Participation of the Double Bonds. Relatively few transformations that take place at the double bonds of 2H-pyrans are known. 2H-Pyrans XXXIX readily add the following dienophiles: tetracyanoethylene [99], maleic anhydride [77, 78, 99], and oxygen [77, 78, 99]. The indicated transformations are described by the following equations:



Similarly, the double bond of 2H-pyran LXX, which exists in equilibrium with its valence isomer LXIX, reacts with maleic anhydride. In addition to cyclic compound LXXI, a product of ring cleavage at the C-O bond, viz., LXXII, is also formed in the hydrogenation of pyran LXX [63]:



Adducts of 2H-pyrans with maleic anhydride are also described in [17, 21, 87]. The reaction of 2,3,4,5,6-pentaphenyl-2H-pyran with oxygen [23] and of 2-alkoxy-2H-pyrans with tetracyanoethylene [32] have been studied. Catalytic hydrogenation over Raney nickel has been used [17, 23, 84, 87, 89] to obtain tetrahydropyrans.

2.3. Reactions with Cleavage of the C-O Bond. Pulse photolysis has shown that reversible cleavage of the C-O bond and the formation of the cis isomer (relative to the γ, δ bond) of dienone XL occur in the irradiation with UV light of solutions of 2H-pyrans XXXII ($R^1 = R^2 = \text{CH}_3, R^3 = \text{CH}_2\text{CO}$ or CH_3OCO) in nonpolar solvents [75, 76].

2H-Pyrans XXXIX undergo thermal isomerization to unconjugated dienones XXXVIII with cleavage of the C-O bond [74].

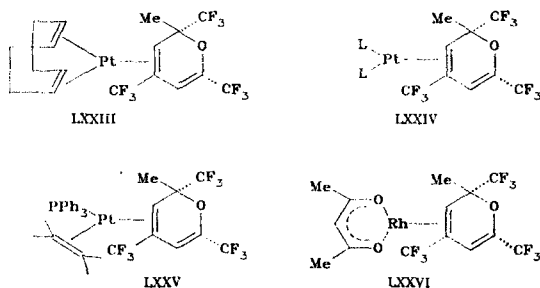
The formation of a product of ring cleavage at the C-O bond is possible in the hydrogenation of some 2H-pyrans over Raney nickel [63, 86].

In [21, 26] it was shown that 2H-pyrans are capable of undergoing isomerization in the presence of Grignard reagents to give butadiene ketones, which react with excess organometallic compound to give tertiary butadiene alcohols.

The reduction of 2H-pyrans XXXVI by complex metal hydrides leads to the formation of conjugated dienols [5]. It is assumed that direct reduction of the carbonyl group of dienones XXXVII, which are valence isomers of the corresponding 2H-pyrans, occurs in this case.

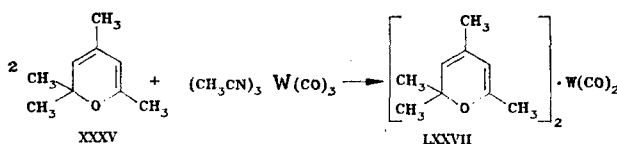
2.4. Preparation of π Complexes. 2-Methyl-2,4,6-tris(trifluoromethyl)-2H-pyran readily forms complex LXXIII upon reaction with bis(cycloocta-1,5-diene)platinum [100]. Under the influence of PPh_3 , LXXIII is converted to complex LXXIVa. Complexes LXXIVb, c are formed by the action on 2-methyl-2,4,6-tris(trifluoromethyl)-2H-pyran of the following trivalent platinum compounds $[\text{Pt}_2(\text{CNR})_6]$ [$R = \text{tert-C}_4\text{H}_9$ or $\text{C}_6\text{H}_5(\text{Me})_2-2,6$]. 2-Methyl-2,4,6-tris(trifluoromethyl)-2H-pyran reacts with $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PPh}_3)]$ to give complex LXXV.

A study of the ^{19}F and ^{13}C NMR spectra shows that the bond between the pyran and platinum is of the η^2 type. In contrast to this, the reaction of 2-methyl-2,4,6-tris(trifluoromethyl)-2H-pyran with $[\text{Ph}(\text{acac})(\text{C}_6\text{H}_4)_2]$ (where acac is acetylacetonate or pentane-2,4-dionate) leads to complex LXXVI, in which a η^4 bond is realized.

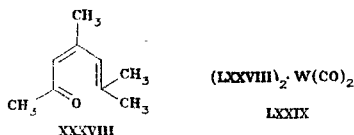


LXXIV a L=PPh₃; b L=*t*-BuCN; c L=2,6-(Me)₂C₆H₃CN

An attempt to obtain π complexes of 2H-pyrans with carbonyls of metals of the adjoining subgroup of group VI elements of the periodic system has been made [101]. Thus black stable crystals, the empirical formula of which corresponds to π complex LXXVII, were isolated in very low yield in the reaction of 2,2,4,6-tetramethyl-2H-pyran (XXXV) with the tris(ace-tonitrile)tungsten tricarbonyl complex in refluxing hexane:



However, in a detailed (IR, NMR, and mass-spectral) investigation of the products of this reaction it was established that a π complex is not formed in this reaction: The valence isomer of XXXV, viz., 4,6-dimethyl-3,5-heptadien-2-one (LXXVIII), and a very small amount of a tungsten dicarbonyl complex (LXXIX) of this isomeric form are detected in the reaction mixture.



3. Spectroscopy of 2H-Pyrans

The UV spectra of 2H-pyrans were studied in [9, 13, 16, 17, 21, 66, 84, 86-89, 91-93, 97]. It was shown that the absorption maxima of 2H-pyrans are found at 235-260 and 290-350 nm.

A band at 1630-1680 cm^{-1} , which is characteristic for C=C bonds, and a band at 1090-1215 cm^{-1} , which is due to vibrations of the ether C-O-C bond, are observed in the IR spectra of 2H-pyrans [5, 9, 13, 16, 17, 20, 21, 35, 66, 87, 89, 91-93, 97, 98].

The PMR spectra of 2H-pyrans were studied in [3, 16, 17, 20, 21, 31, 35, 51, 62-64, 68, 85-87, 92, 95, 97, 98]. This method was used, in particular, to study the valence isomerism of 2H-pyrans [62-64].

Some 2H-pyrans have been studied by means of ^{13}C NMR spectroscopy [20, 33, 67, 68, 97].

Data from ^{19}F NMR spectroscopy have been presented for fluorine-containing 2H-pyrans [97, 98]. The π complexes obtained on the basis of 2,4,6-tris(trifluoromethyl)-2H-pyran have also been studied by this method [100]. Kitazume and co-workers [98] have studied the mass spectra of 2H-pyrans LXIII-LXVI.

CONCLUSION

An analysis of the literature data provides evidence that rather reliable methods for the synthesis of 2H-pyran derivatives have been developed, although the methods for the preparation of the parent compound of the 2H-pyran series are still not precise because of its low stability. The widely used method of fixation of unstable molecules as a result of complexing [102] is apparently unsuitable in this case, since the ligand exists in the dienone isomer form in the complexes [101].

With the exception of valence isomerism, virtually no study has been devoted to the physicochemical properties of 2H-pyrans. A relatively small amount of data on the complex-

ing capacities of compounds of this class is available. Judging from the available information, they should display the properties of π -donor ligands. Cryochemical methods [103, 104] may evidently prove to be useful with respect to attempts to synthesize π complexes from them. Moreover, one cannot exclude the possibility that the oxygen atom may participate [106] in complexing with Pearson hard acids [105], particularly when the reaction under consideration will be accompanied by opening of the pyran ring.

Of extreme promise, in our opinion, are studies of the recyclizations of 2H-pyrans, further studies of reactions with the participation of the double bonds, reactions involving cleavage of the C-O bond, etc. These transformations may be valuable methods for the preparation of compounds of the aromatic and aliphatic series that are difficult to obtain by other methods, as well as diverse cyclic compounds with complex structures.

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SYNTHESIS OF 4,5-DIHYDROFURAN DERIVATIVES. STEREOCHEMICAL
STUDY OF THE REACTIONS OF 1,3-ALKADIENES WITH β -DICARBONYL
COMPOUNDS*

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4,5-Dihydrofuran derivatives were obtained by the reaction of *cis*- and *trans*-1,3-alkadienes with carbonyl compounds in the presence of the manganese(III) acetate/copper(II) acetate oxidizing system. It was observed that in the case of *cis*-1,3-alkadienes, in contrast to *trans*-1,3-alkadienes, inversion of the *cis* double bond, the degree of which depends on the structures of the unsaturated and carbonyl components of the reaction, occurs. It was shown that the reaction of *cis*-1,3-dodecadiene with diethyl malonate leads to the corresponding 1,4-addition product.

The study of the reactions of unsaturated compounds with α -oxo- and α,α -dioxoalkyl radicals generated by oxidation of carbonyl compounds by manganese(III) acetate has proved to be extremely fruitful in a synthetic respect [2-13]. In particular, the reaction of 1,3-alkadienes with dicarbonyl compounds is a preparative method for the synthesis of 4,5-dihydrofuran derivatives [14-16]. A stepwise mechanism that includes the following steps has been proposed for reactions of this type: 1) the formation of a complex of the dicarbonyl compound with manganese(III) acetate; 2) ligand formation with the 1,3-alkadiene; 3) addition of the carbonyl compound to the 1,3-alkadiene in the coordination sphere of the manganese(III) ion; 4) dissociation of the allyl complex at the Mn-C bond to give an allyl radical and a manganese(II) ion; 5) oxidative cyclization of the allyl radical under the influence of copper(II) acetate [16]. This reaction scheme is hypothetical and should be refined on the basis of research specially designed to ascertain specific aspects of the mechanism. In particular, it seemed of interest to use a stereochemical test: separate subjection to the reaction of the *cis* and *trans* isomers of 1,3-alkadienes in order to detect the possible inversion of the C₃-C₄ double bonds during the process.

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