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The Interconversions of Pyrylium Salts, Pyrans, Pyrones, and Their Open-chain Forms

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A general scheme is proposed for the interconversions of six-membered oxygen-containing heterocylces (pyrylium salts, pyrans, and pyrones) and their open-chain forms, having selected pyrylium salts as compounds of the key type. The latest data concerning the mechanism of a number of the above transformations are examined. It is shown that ring opening is one of the most characteristic manifestations of the reactivity of six-membered oxygen-containing heterocylces.
The bibliography includes 231 references.

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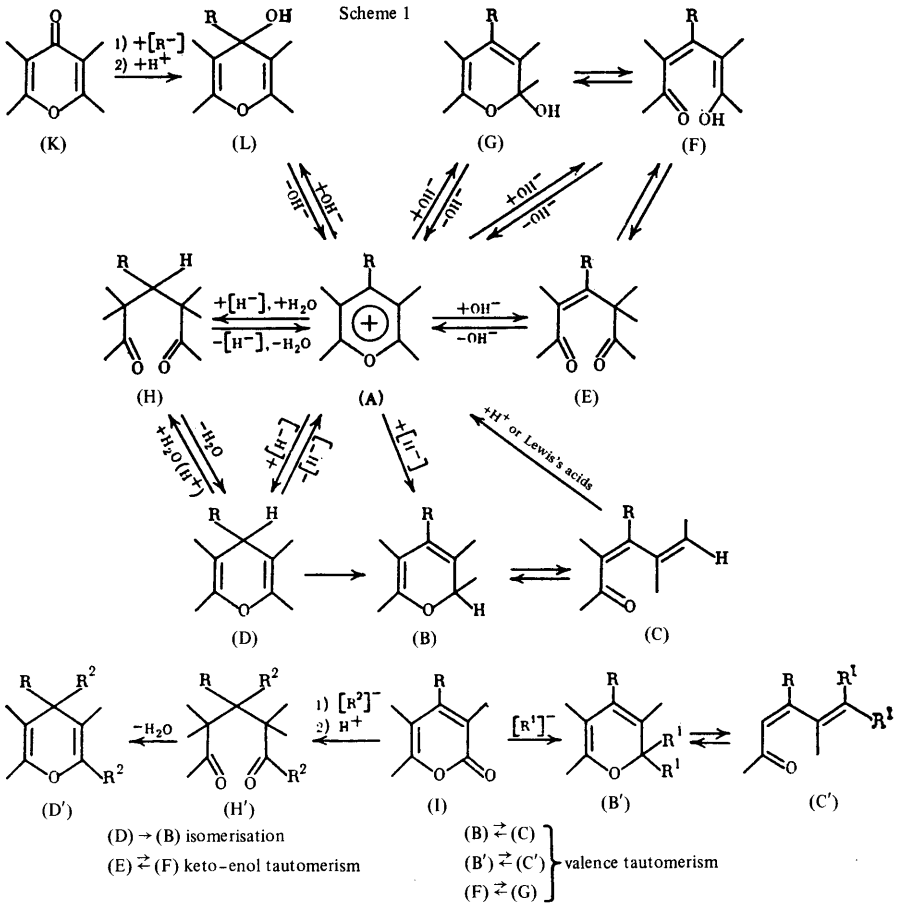
I. INTRODUCTION

Six-membered oxygen-containing aromatic and non-aromatic heterocycles (pyrylium salts, 2*H*- and 4*H*-pyrans, α- and γ-pyrones, and α- and γ-pyranols) and their open-chain forms (pentene-1,5-diones, pentadien-5-ones, pentane-1,5-diones, etc.) are readily interconverted. Individual aspects of these reactions have been the subject of studies since the beginning of this century, but investigation of the problem in terms of the complete set of its general and specific properties has become possible only recently. This has been promoted, particularly, by the application of physicochemical methods (spectroscopic and electrochemical) in practical chemical studies, by the investigation of kinetics, and also by the expansion of synthetic possibilities, for example, as a result of the vigorous application of organometallic compounds.

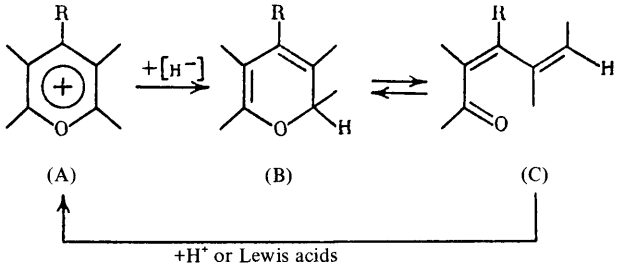
In the present review we propose a general scheme for the above reactions involving a fundamental class of heterocycles, namely pyrylium salts[1-14] (Scheme 1), as compounds of the key type. In the course of the exposition we shall deal with individual fragments of this scheme which reflect the most characteristic transitions undergone by the classes of compounds included in it†.

† In view of the complexity of the structures of the 1,5-diketones (H′) and 2*H*-pyrans (B′) formed, which are incapable of participating in the majority of the reactions considered, the transitions (I)–(H′) and (I)–(B′) are included in addition to the main scheme. We may point out, however, that diketones of type (H′) are capable of being dehydrated to 4,4′-disubstituted 4*H*-pyrans (D′) and 2*H*-pyrans (B′), which can undergo valence isomerisation to the *cis*-dienones (C′). In order to simplify Scheme 1 the addition and elimination of a hydride ion are considered in the case of the (A)–(D) transition, while the reactions of pyrilium salts with other compounds, leading to 4*H*-pyrans with a more complex structure, are dealt with in the text. Similarly the scheme indicates only the effect of the hydride ion for the (A)–(D) transitions. Other instances of the synthesis of 2*H*-pyrans on the basis of pyrylium salts are described in the text. The OH^- anion has been adopted as the effective species in the (A)–(L), (A)–(E), (A)–(F), and (A)–(G) transitions; more complex examples involving alkoxy-groups are discussed in the text.

Scheme 1



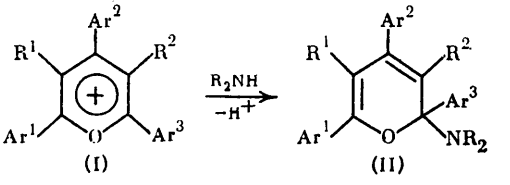
II. PYRYLIUM SALTS–2*H*-PYRANS–*cis*-DIENONES



Alkali metal tetrahydroborates ($NaBH_4$, $LiBH_4$, and KBH_4) react with pyrylium salts to form unstable 2-monosubstituted 2*H*-pyrans (B),[15–20] which rapidly isomerise to the corresponding *cis*-dienones (C). It is striking that in all cases the interaction of complex metal hydrides with pyrylium salts leads to the formation, together with the above compounds, also of 4*H*-pyrans (D) and their open-chain forms—saturated 1,5-diketones.[3]

Comparatively stable 2*H*-pyrans of type (B) and their valence tautomers, i.e. *cis*-dienones (C), are synthesised also by the reaction of pyrylium salts (A) with organometallic reagents (not included in the Scheme).[21–31]# Since the positive charge on the pyrylium cation is concentrated in the 2-, 4-, and 6-positions, as has been confirmed by quantum-chemical calculations,[12,14] 4*H*-pyrans are formed together with 2*H*-pyrans. The ratios of the products formed (2*H*-pyrans, *cis*-dienones, and 4*H*-pyrans) are determined by the structure of the pyrylium salt, the nature of the nucleophile, and the reaction conditions.

When pyrylium salts (I) are treated with dialkylamines in aprotic solvents (for example in diethyl ether), stable 2*H*-pyran derivatives (II) can be isolated in a crystalline form:[36]

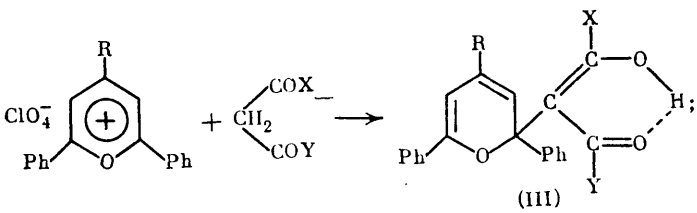


R^1 = H, Me; R^2 = Me .

#2*H*-Pyrans[32] can also be obtained by treating α-pyrones with organometallic reagents (Section IX), in the course of the isomerisation of 4*H*-pyrans (Section IV), and as a result of cyclocondensation[33–35] with participation of carbonyl compounds.

The authors[36] explained the stability of the 2*H*-pyrans (II) by the presence of substituents in the 3- or 3- and 5-positions in the pyrylium ring.

Pyrylium salts are also capable of reacting with CH acid compounds to form 2*H*-pyran derivatives. They are formed, for example, in the reaction of 2,4,6-triphenylpyrylium tetrafluoroborate with acetonedicarboxylic acid or acetylacetone.[4] The method of phase-transfer catalysis provides much greater possibilities for the synthesis of 2*H*-pyrans involving CH acid compounds.[37] 2*H*-Pyrans (III, a–g) have been obtained by this method in the reaction of 2,4,6-triphenyl and 2,6-diphenyl-4-(α-thienyl)-pyrylium perchlorates with acetoacetic ester, acetylacetone, and malonic ester:



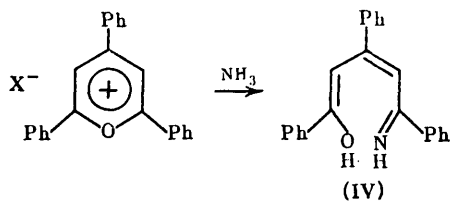
(III)

(a) R=Ph, X = Me, Y=OEt, (b) R=Ph, X=Y=Me, (c) R=Ph, X=Y=OEt; (d) *R*= , X=Y=OEt .

The isolation of the 2*H*-pyrans (III, a–g) confirms the mechanism proposed previously[5] for the reaction of pyrylium salts with active methylene groups in which the intermediate formation of 2*H*-pyrans was postulated. One of them, namely compound (Ib), has been isolated[15] in the reaction of 2,4,6-triphenylpyrylium tetrafluoroborate with acetylacetone in the presence of 1 mole of potassium t-butoxide, but its structure has not been rigorously confirmed.

The appearance of 2*H*-pyrans of type (B) is usually postulated as the first stage in the interaction of pyrylium salts (A) with various nucleophiles, leading either to recyclisation products[11–14] or to ring opening products.[8,14]§ The latter are frequently intermediates in the recyclisation of pyrylium salts; if these products are stable, the reaction terminates with their formation. The reactions of 2,4,6-trisubstituted pyrylium salts with N-containing and certain other nucleophiles, in which ring-opening products with different stabilities can be obtained, are examples of the second of the competing processes indicated.

Thus the reaction of a pyrylium salt with ammonia can lead to the isolation of the ring opening product—the relatively unstable iminoenol (IV):[38]

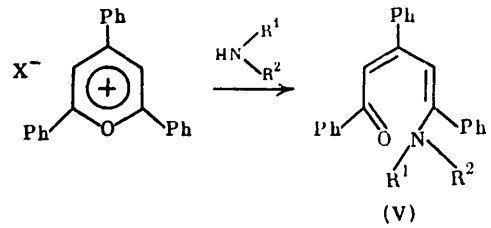


(IV)

When pyrylium salts are acted upon by amines, there is a possibility of the formation of aminopentadienones (V).[39,40]

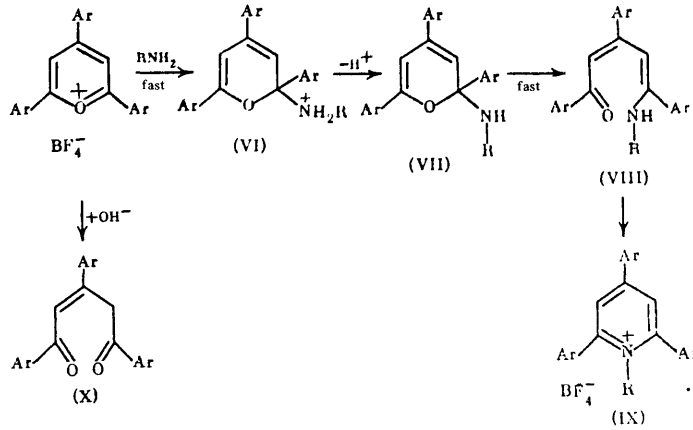
§ These products can be regarded as derivatives of the diketone forms of the pseudobases of pyrylium salts formed via the keto-groups.

In the case of primary amines the yields of compound (V) are low, while in the reaction involving secondary amines they are satisfactory:



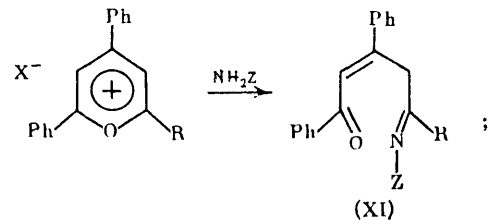
(V)

The interaction of pyrylium salts with amines has been studied in detail by Katritzky and co-workers.[41,42] The reaction pathway and the structure of the substances formed were studied, in particular, by ^{13}C NMR:



When two moles of a primary amine are introduced into the reaction, pyridinium salts (IX) are formed in quantitative yields, but, when less than two moles of the amine is used, the amount of the side product, the unsaturated diketone (X), increases. Under the reaction conditions, the latter also gives rise to a pyridinium salt, but this reaction is very slow. The authors[42] assume that the second amine molecule is necessary to abstract a proton from the intermediate (VI). The pyrylium salt which failed to react is converted by traces of water into the pentenedione (X). In particular, the reactions with n-butylamine and benzylamine take place in this way. Pyrrolidine and piperidine have been used as secondary amines. The reaction of pyrylium salts with 2 moles of a secondary amine leads to the formation of aminopentadienones of type (VIII), which do not cyclise to pyridinium salts.

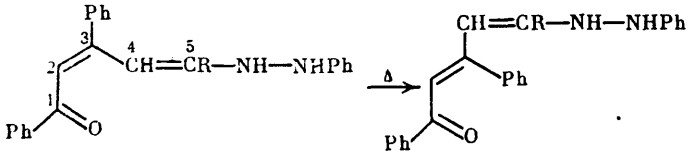
The fairly stable monoxime (XIa) and the monophenylhydrazone (XIb) are formed when a pyrylium salt interacts with hydroxylamine[43] and phenylhydrazine:[43,44]



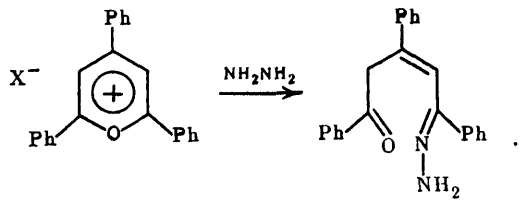
(XI)

(a) R=Ph, Z=OH; (b) R=Ph, Me; Z=NHPh .

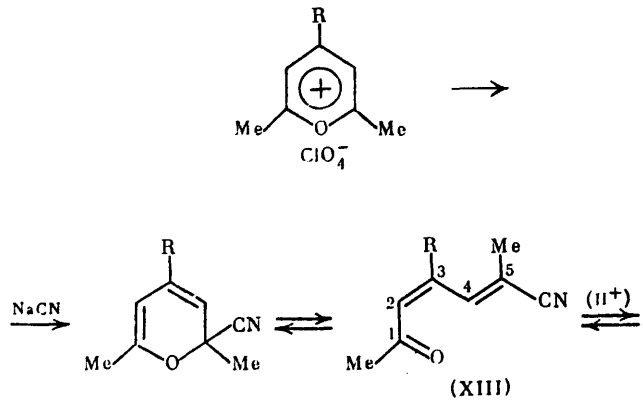
The monophenylhydrazone (XIb) is also formed as the *cis*-isomer [with a *cis*-disposition the carbonyl group and the CH=CR–NH–NHPh group relative to the C(2)=C(3) double bond], which is converted into the *trans*-isomer on refluxing in a neutral medium (ethanol):



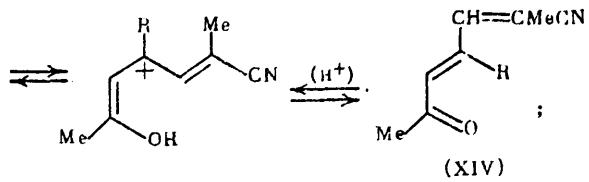
When the 2,4,6-triphenylpyrylium salt is acted upon by hydrazine hydrate, the unstable monohydrazone (XII) is formed:[45,46]



(XII)



(XIII)

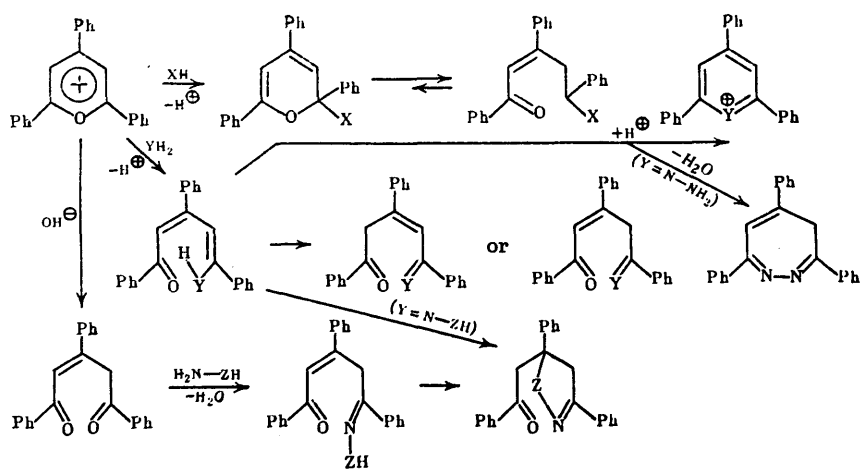


(XIV)

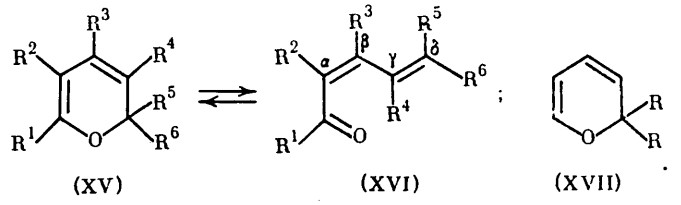
R = Me, Et.

The ring opening products in the reaction of 2,4,6-trialkylpyrylium salts with cyanides are the *cis*-cyanopentadienones (XIII). On treatment with concentrated inorganic acids, the latter react via two pathways: they are reconverted into the initial pyrylium salt, liberating hydrogen cyanide, and they isomerise to the *trans*-pentadienones (XIV). The *cis,trans*-isomeric forms are determined by the relative positions of the carbonyl group and the CHCMeCN group relative to the C(2)=C(3) double bond:[47,48]

The products of the opening of the ring in pyrylium salts, which can also be regarded as the open-chain forms of 2*H*-pyrans, are capable, as already stated above, or different types of subsequent cyclisation with formation of various heterocyclic systems. For example, compounds (IV), (V), (XIa), (XIb), and (XII) cyclise with formation of the corresponding nitrogen-containing heterocycles—pyridine, pyridinium salts, isoxazole, pyrazoles, and diazepine, as shown in the general scheme published by Balaban and Silan:[49]



The phenomenon of valence isomerism, a symmetry-allowed thermal pericyclic process[52] with a low activation energy, is characteristic of the class of 2*H*-pyrans.[50,51] It results in the establishment of a rapid and reversible equilibrium between the 2*H*-pyrans (XV) and their valence tautomers—the *cis*-dienones (XVI)¶:[53–79]



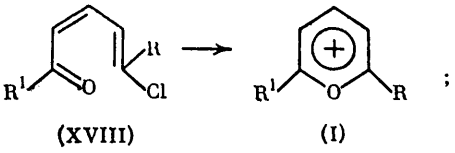
(XV) (XVI) (XVII)

For this very reason, the parent compound of the class of 2*H*-pyrans, namely unsubstituted pyran, has not so far been obtained. Quantum-chemical calculations of the stability of the valence isomers (XV) and (XVI) [80–83] give preference to the cyclic form (XV). In the course of the analysis of the pathways leading to the valence photo- and thermo-isomerisation of the 2*H*-pyran ring, taking into account the characteristic features of the electronic structure of the transition state in the reaction

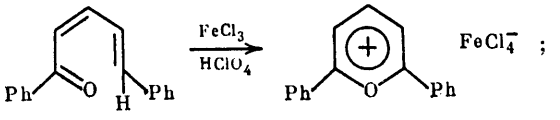
$$(XV) \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} (XVI),$$

a correspondence has been observed between the energy barrier to the opening of the pyran ring and the C_{sp^3}–O bond length.[83] At the same time *ab initio* calculations have shown that open-chain forms with different geometries are more stable for both the 2*H*-pyran (XVII, R = H) [80] and its diemthyl derivative (XVII, R = Me).[82]

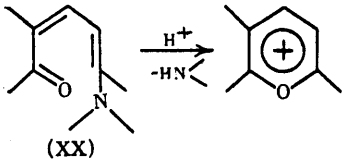
The reverse transformation of 2*H*-pyrans into pyrylium salts (A), which is characteristic of 4*H*-pyrans (D), has not been observed in the case of the 2*H*-pyran (B). However, compounds which are derivatives of dienones, for example, (XVIII)–(XXI), readily cyclise with formation of pyrylium cations:[60,84–87]



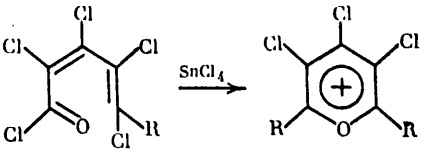
(XVIII) (I)



(XIX)

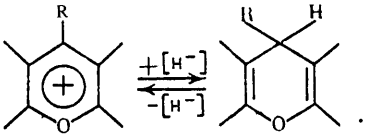


(XX)



(XXI) $SnCl_5^-$

III. PYRYLIUM SALTS–4*H*-PYRANS



(A) (D)

The transformation of pyrylium salts (A), usually with a free γ-position (R = H), into 4*H*-pyrans (D) constitutes the most thoroughly developed method of synthesis of the latter and is achieved by reduction with complex metal hydrides.[26–31,88–91] However, the methods of synthesis of 4*H*-pyrans from pyrylium salts are not restricted to this simplest case. 4-Substituted or 4,4'-disubstituted 4*H*-pyrans are also formed as a result of reaction with CH acid compounds in the presence of catalysts,[15,92–94] by reaction with organic and inorganic nucleophiles in the absence of catalysts,[95–105] with the aid of organometallic synthesis,[106–122] and by many other procedures.[123–127] The reaction of 2,4,6-trisubstituted pyrylium salts with strong nucleophiles (Grignard reagents, organolithium compounds, or complex metal hydrides) results in the formation, together with 4*H*-pyrans (D), of 2*H*-pyrans (B) and their valence isomers—*cis*-dienones (C). In an acid medium the open-chain form of the 4*H*-pyran, namely a saturated 1,5-diketone, is isolated instead of the 4*H*-pyran itself.

The reduction and dimerisation of pyrylium salts under the influence of electron donors lead to the formation of bis-4*H*-pyrans.[111,128–130]†

4*H*-Pyrans[120] are compounds of a comparatively unstable type. The unsubstituted 4*H*-pyran, which was obtained as late as 1962 from glutaric dialdehyde,[144] is a colourless liquid, which rapidly decomposes in the light at room temperature.[144,145] The introduction of substituents stabilises the pyran ring, but in this case they are frequently isolated in

¶ The dienones can exist as the *cis*- or *trans*-isomers with respect to the αβ-double bond.[44,48,75] It has been shown that only one geometrical isomer is involved in the dienone–2*H*-pyran equilibrium.[18,75] From this and also from the hypothesis that the valence isomerisation can involve only the geometrical isomer with the minimum distance between the C=O group and the C_δ atom, it has been concluded[75] that this isomer exists in the *cis*-form. Direct observation by means of ^{1}H NMR has confirmed this claim, which had been accepted previously without adequate evidence.[66,68,70,71]

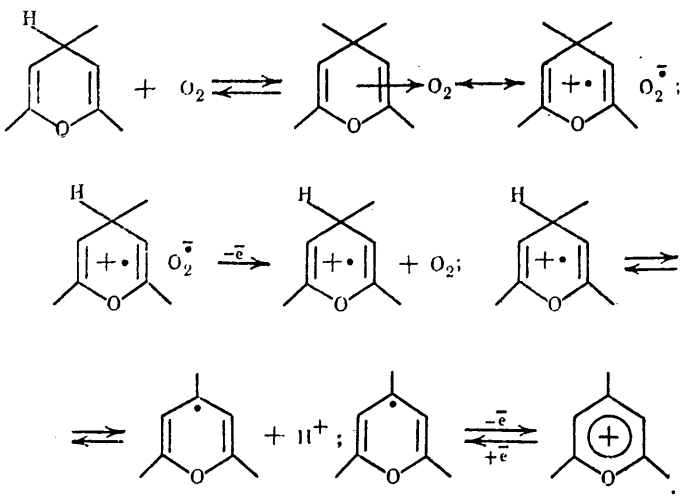
† Apart from the synthesis from pyrylium salts, 4*H*-pyrans can be obtained also by condensation involving carbonyl compounds[131–143] and by the cyclisation of 1,5-dicarbonyl compounds.[117,131,145]

the form of non-crystalline oils which are difficult to purify.[4, 16,89,107,110,111,131] On storage, many crystalline pyrans "deliquesce", but 4*H*-pyrans with carbaboranyl substituents are more stable.[113–121]

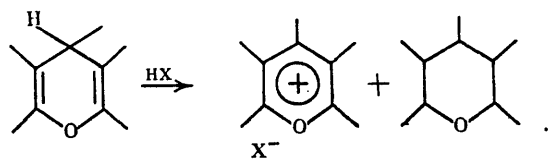
4*H*-Pyrans (D), containing a hydrogen atom in the γ-position and therefore capable of undergoing oxidative dehydrogenation, serve as convenient starting materials in the synthesis of pyrylium salts (A). 4*H*-Pyrans are dehydroaromatised with the aid of acetyl perchlorate,[108–111,115,117,119,120] triphenylmethyl perchlorate,[99,102,103,121,122,125] PCl_5,[117,125] $FeCl_3$,[4] CCl_3,[110,111,120] 2,4,6-tri-t-butylcyclohexadienone,[110,111] the tris(*p*-bromophenyl)aminium radical-cation,[110–114,116,117,120] benzenediazonium tetrafluoroborate,[110,111] tropylium tetrafluoroborate,[88] bis(2,4-dimethoxyphenyl)immonium perchlorate,[115,116,120] etc.

The transfer of a hydride ion is observed in almost all classes of organic compounds and has been the subject of controversy.[146,147]

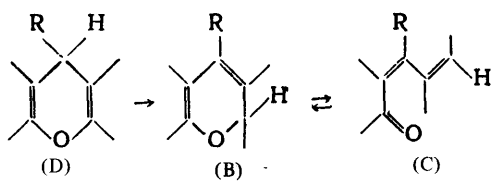
Okhlobystin and co-workers[148] investigated the dehydroaromatisation of pyrans by EPR and electrochemically; they also proposed a stepwise mechanism for this process, which is vigorously catalysed by oxygen. They suggest that the substrate undergoes one-electron oxidation in the decisive stages:



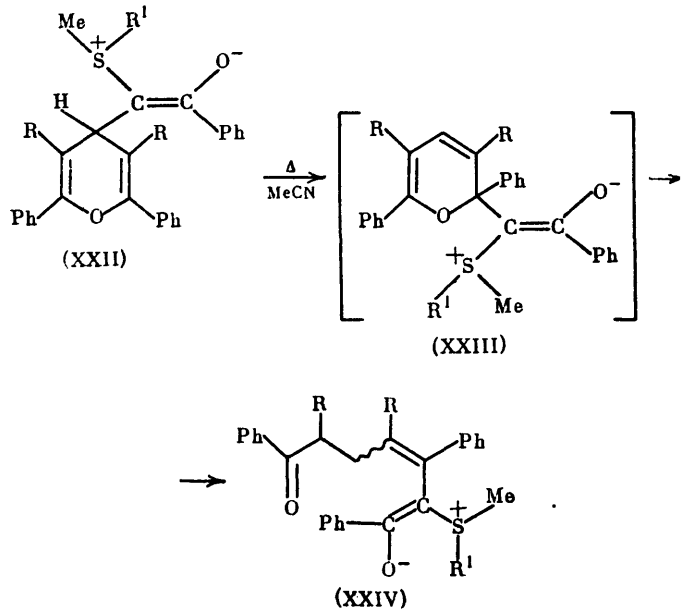
The ability to disproportionate under the influence of acids (protic and aprotic), which results in the formation of a pyrylium salt and a tetrahydropyran, is also characteristic of 4*H*-pyrans:[149,150]



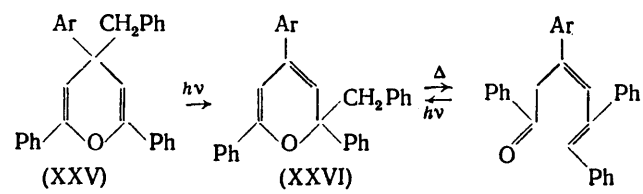
IV. 4*H*-PYRANS–2*H*-PYRANS–*cis*-DIENONES



4*H*-Pyrans (XXII)#, containing an ylide group in the 4-position, give rise to the open-chain compounds (XXIV) in the form of two geometrical isomers in the course of their thermal rearrangement.[151] There is no doubt that the first stage in the rearrangement involves the formation of 2*H*-pyrans (XXIII), which then undergo valence isomerisation to the corresponding dienones (XXIV):



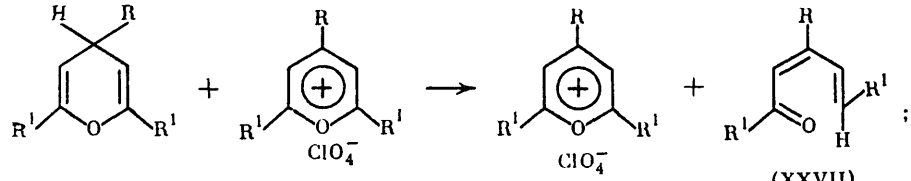
When the 4*H*-pyrans (XXV), containing the benzyl group in the γ-position, are irradiated, they readily give rise to the corresponding 2*H*-pyrans (XXVI):[152–155]



The 2*H*-pyrans (XXVI) undergo thermal isomations to non-conjugated dienones, which recyclise to the 2*H*-pyrans on irradiation. The migration of the benzyl group on photoisomerisation of 4*H*-pyrans proceeds via a singlet mechanism. The positions of the double bonds and of the substituting groups in the isomeric heterocycle are indicated by its ability to react with maleic anhydride, to form a transannular peroxide on sensitised photochemical oxidation, etc.

The hydride mobility of 4*H*-pyrans in relation to 2*H*-pyran and its open-chain isomer (a dienone) has been investigated;[90] pyrylium cations were used as hydride ion acceptors. Treatment of 2,6-triphenyl-4*H*-pyrans with the corresponding pyrylium cation leads to the formation of cinnamylideneacetophenone (XXVIIa) and 1,3,5-triphenylpenta-2,4-dienone (XXVIIb):

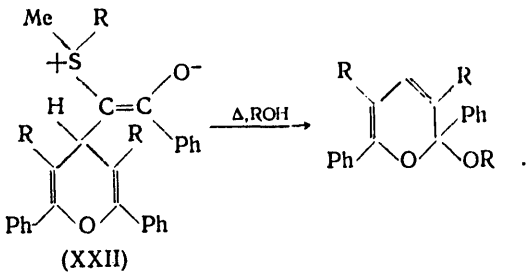
#The isomerisation of the 4*H*-pyrans (D) to 2*H*-pyrans (B) is given a conventional representation in Scheme 1, since it has been simplified by indicating hydrogen as the migrating species.



(a) R^1 = Ph, R = H; (b) R = R^1 = Ph.

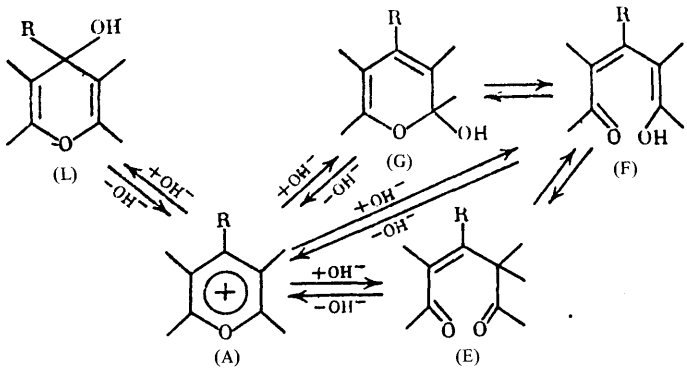
Thus it has been shown that the 2*H*-pyran is formed in the hydride transfer from the 4*H*-pyran to the 2-position in the pyrylium ring. On valence isomerisation, the 4*H*-pyran gives rise to the more stable open-chain form. In other words, 4*H*-pyrans (D) are less stable than 2*H*-pyrans (B), which are in their turn less stable than their isomeric *cis*-dienones (C).

The thermal rearrangement of the 4*H*-pyrans (XXII), containing the sulphonium ylide group in the γ-position, in methanol or ethanol results in the formation of the corresponding alkoxy-2*H*-pyrans:[151]



(XXII)

V. PYRYLIUM SALTS–PSEUDOBASES OF PYRYLIUM SALTS

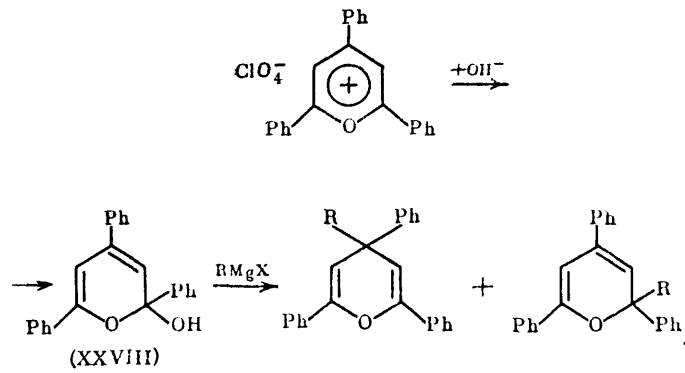


The products of the addition of *O*-nucleophiles (hydroxide and alkoxide anions) to the α- and γ-positions in pyrylium salts are referred to as the pseudobases (E)–(G) and (L).[156] Stable pseudobases have been obtained from arylpyrylium salts. Alkylpyrylium salts give rise to sensitive and unstable pseudobases, which cannot be isolated. The crystalline 4-methyl-2,6-di-t-butylpyrylium pseudobase, which can be stored for several minutes at room temperature, is an exception.[12]

The structure of the substances formed on reaction of pyrylium salts with *O*-nucleophiles is determined mainly by the structure of the initial pyrylium cations and also by the character of the reagent and has been established unambiguously only recently when spectroscopic methods (infrared, ultraviolet, and NMR spectroscopy) and X-ray diffraction methods have become available.

The first stage in the reaction of pyrylium salts with the hydroxide anion, like that in the reactions with other nucleophiles, may involve the attack on the α- or γ-position with formation of the 4-pyranol (L) or the 2-pyranol (G), which is then converted into the pentene-1,5-dione (E) (in the *cis*- or *trans*-form) or the enolic tautomer (F)§.

The hydrolysis of 2,4,6-triphenylpyrylium perchlorate in a highly alkaline medium (pH 14) yielded the corresponding α-pyranol (XXVIII)[157] in conformity with the fact that the α-positions are more reactive:[12]



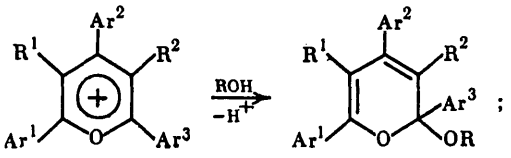
(XXVIII)

The concentration of hydroxide ions was kept constant by means of a buffered methanolic solution. On reaction with organometallic reagents, the α-pyranol produces substituted 2*H*- and 4*H*-pyrans.

The formation of 2-methoxy-2*H*-pyrans on interaction of pyrylium salts with the methoxide anion has been demonstrated by kinetic methods[158,159] and also by ^{1}H NMR[160] and ^{13}C NMR.[42] 4-Methoxy-4*H*-pyran is formed together with 2-methoxy-2*H*-pyran.[158,159] There is also a possibility of the formation of the corresponding *cis*-dienone instead of 2-methoxy-2*H*-pyran.[158,159] The ratio of the above products is determined by the structure of the initial pyrylium salt and the reaction conditions. For example, it has been shown that 2,4,6-triarylpyrylium salts having substituents in the 3- or 3- and 5-positions in the pyrylium ring give rise to stable crystalline 2-alkoxy-2*H*-pyrans on treatment with alkali metal alkoxides:[161]

---

§Because of the conventional nature of the general scheme (1), the OH^- anion has been adopted as the O-nucleophile in the fragments having a bearing on the formation of the pseudobases in order to demonstrate in a more clear-cut form the possibilities for the interconversions of compounds (A), (E), (F), (G), and (L).

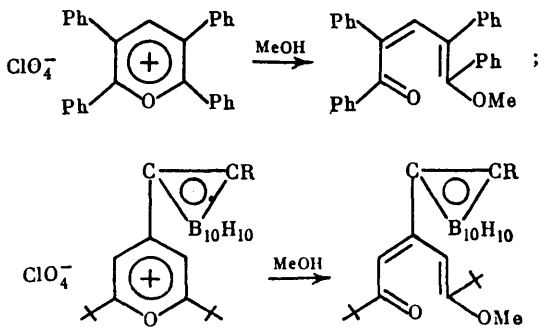


R^1 = H, Me; R^2 = Me, $PhCH_2$.

However, as a rule open-chain forms (pentene-1,5-diones or ketodienols) are formed in the course of hydrolysis or alcoholysis. The hydrolysis of, for example, 2,3,5,6-tetraphenylpyrylium[162] and 2,6-di(methoxycarbonyl)pyrylium[163] cations is carried out in an aqueous medium. However, the formation of open-chain forms of the pseudobases is usually observed in hydrolysis in the presence of inorganic and organic bases.

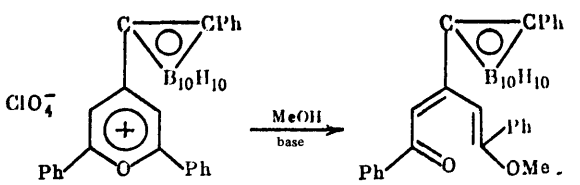
Although the formation of ketodienols is relatively uncharacteristic of pyrylium salts, nevertheless, when the latter are acted upon by alkoxides in the corresponding alcohols, the ketodienol ethers are formed readily. For example, the 2,4,6-triphenylpyrylium cation gives rise to oily methoxy- and ethoxy-derivatives as well as the crystalline isopropoxy-derivative.[49]

2,3,5,6-Tetraphenylpyrylium[162] and 2,6-di-t-butyl-4-carbaboranylpyrylium[164–166] perchlorates readily produce the corresponding stable methyl ethers of ketodienols in the course of methanolysis:



R = Me, Ph.

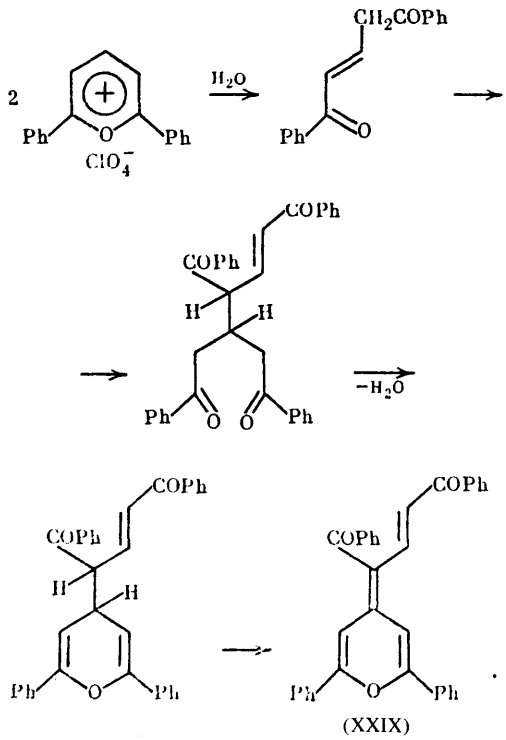
The methanolysis of 2,6-diphenyl-4-(phenyl-*o*-carbaboranyl)pyrylium perchlorate, which leads to the methyl ether of the ketodienol, takes place only in the presence of bases:



The bases used are $NaHCO_3$, MeONa, Et_3N, 5-aminotetrazole, $H_2NC_6H_4COOEt$, NH_2CONH_2, $(PhNH)_2C{=}NH$, $Me_2C{=}NOH$, and Br=NPh [?(Ed.of Translation)].

The formation of the methoxide anion, which has fairly pronounced nucleophilic properties,[167] is apparently induced by various types of acid–base interaction (autoprotolysis of the alcohol, protonation of the amine, etc.). The attack on the pyrylium ring is then undoubtedly facilitated by the electron-accepting effect of the carbaboranyl substituent; cations containing t-butyl groups in the 2- and 6-positions are especially activated.

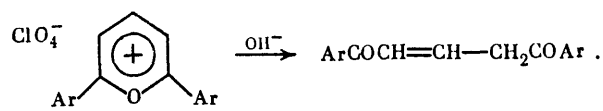
The hydrolysis and alcoholysis of 2,6-diarylpyrylium salts with a free γ-position occupies a special place. On interaction with water in the presence of bases, 2,6-diphenylpyrylium perchlorate affords 1,5-diphenyl-4-(2,6-diphenyl-4-pyranylidene)pent-2-ene-1,5-dione.[168,169] The mechanism of the formation of this compound involves the hydrolysis of the pyrylium salt to an unsaturated diketone, which undergoes Michael self-condensation; the subsequent cyclisation to the 4*H*-pyran and dehydrogenation lead to the pyranylidenediketone (XXIX):



(XXIX)

A similar reaction is common to 2,6-diarylpyrylium salts. The optimum conditions for the syntheis of pentenediones of type (XXIX) involve brief refluxing of an equimolar mixture of 2,6-diarylpyrylium perchlorate with water and pyridine in acetonitrile.

Unsaturated 1,5-diketones having the *trans*-configuration were obtained only on treating 2,6-diarylpyrylium perchlorates with an aqueous acetone solution of alkali:



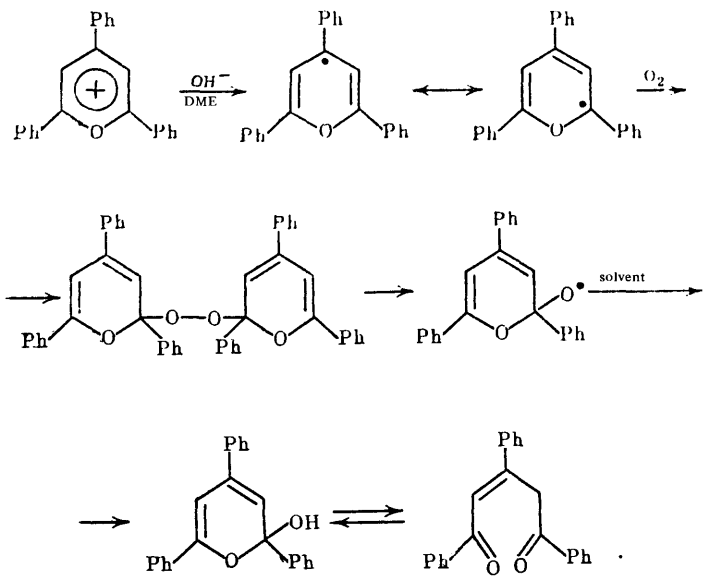
On treatment of 2,6-diarylpyrylium salts with aqueous alcoholic solutions of bases, unstable α-alkoxypyrans are formed; 3-benzoyl-6-ethoxy-6-(*p*-nitrophenyl)-2-phenylpyran was isolated in an analytically pure state. The use of sodium acetate as the base entailed the formation of a complex mixture of acetoxypyrans, whose treatment with acids produced high yields of pyrylium salts with various anions.

The elucidation of the mechanism of the hydrolysis of pyrylium salts leading to the opening of the pyrylium ring is of significant interest. Kinetic methods have been used in a number of studies.[170–172]

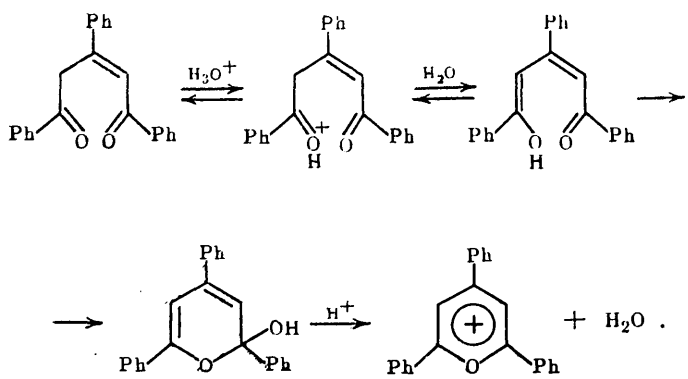
It has been found[173,174] that, on treatment with NaOH in acetone or dimethoxyethane (DME) in the absence of oxygen, 2,4,6-triphenylpyrylium perchlorate is quantitatively converted into the 2,4,6-triphenylpyranyl free radical, which was identified by EPR.

On contact of the reaction mixture with atmospheric oxygen, 1,3,5-triphenylpent-2-ene-1,5-dione is formed. The same diketone has been obtained on oxidising with atmospheric oxygen the free radical arising in the dissociation of the triphenylpyranyl radical dimer.[111]

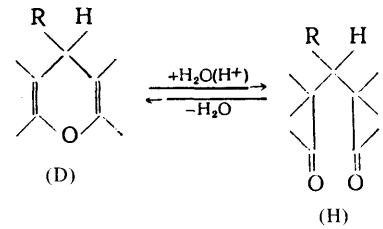
From their data, the authors[173,174] put forward the following mechanism of the formation of unsaturated 1,5-diketones from pyrylium salts:



On treatment with acids, unsaturated 1,5-diketones readily cyclise to pyrylium salts.[41] Kinetic studies of the mechanism of the reactions of the above diketones with H_3O^+ showed that the dione cyclises as a result of the rapid enolisation and subsequent ring closure of the enol to form an unstable 2-hydroxy-2*H*-pyran, which is converted into a pyrylium salt in the presence of protic acid:[175]

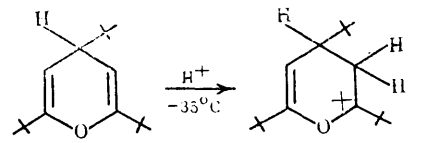


VI. 4*H*-PYRANS–SATURATED 1,5-DIKETONES



4*H*-Pyrans (D)¶ readily undergo ring opening in the course of hydration in an acid medium with formation of saturated 1,5-diketones (H).[16,93,117–120,132,133,163,176–179] Aqueous, alcoholic, or aqueous alcoholic solutions of HCl are then used as a rule and the employment of the strong perchloric acid is essential only for carbaboranyl-4*H*-pyrans.[117–120]

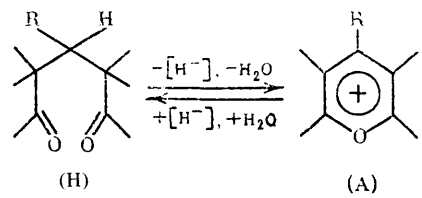
The reaction involving the opening of the pyran ring begins most probably with the protonation of the β-position of the 4*H*-pyran with subsequent addition of the hydroxide anion to the tertiary carbonium ion centre arising in the α-position. For example, it has been shown that the protonated form of 2,4,6-tri-t-butyl-4*H*-pyran, arising in a $FSO_2OH–CS_2$ mixture at −35 °C, gives rise to a well resolved ^1H NMR spectrum, indicating the non-equivalence of the methylene protons in the 3-position:[111]



The reverse reaction involving the cyclisation of the pentane-1,5-diones (H) to the corresponding 4*H*-pyran (D) has been described.[117,131,145,163,176,177,179]

Despite the fact that, on treatment with acids, δ-diketones in general tend to undergo intramolecular aldol condensation with formation of cyclohexenone derivatives, γ-pyran derivatives are formed in many instances where this is allowed by structural factors. This reaction takes place on treatment with P_2O_5,[176] concentrated H_2SO_4,[163,173] and $ZnCl_2$,[131] but saturated carbaboranyl-1,5-diketones readily cyclise even at room temperature in acetic anhydride.[119,178,179]

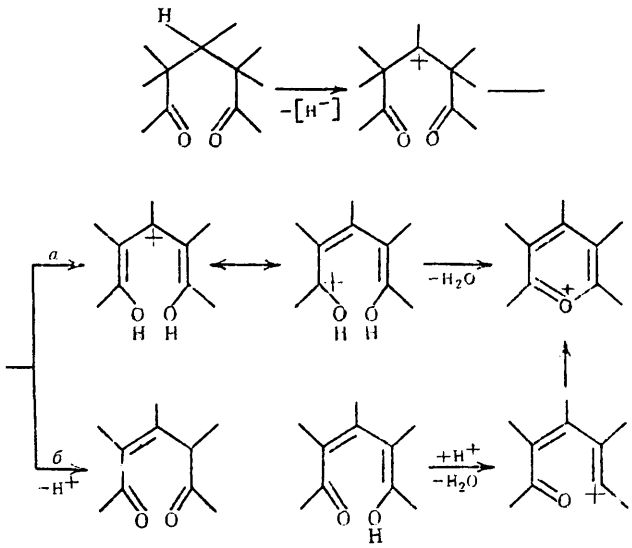
VII. SATURATED 1,5-DIKETONES–PYRYLIUM SALTS



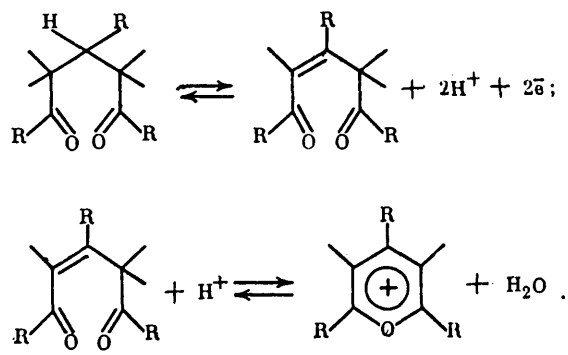
The conversion of saturated 1,5-diketones (H),[180,181] having a hydrogen atom at the C(3) atom, into pyrylium salts (A) is one of the most thoroughly investigated and most widely used methods of synthesis of pyrylium salts. An

¶ Analogous reactions are possible also for compounds (H') and (D') (Scheme 1).

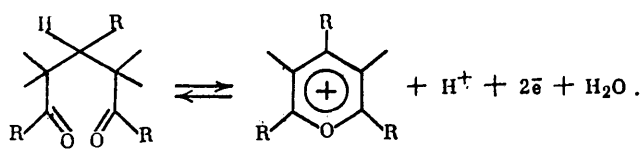
extensive compilation of the reagents used for this purpose has been published in reviews.[6,180] Since two processes take place in the course of thise reaction, namely dehydrogenation and dehydration, the question of the nature of the intermediate remained controversial for a long time. There were two hypotheses; according to the first, an unsaturated diketone is formed initially and then undergoes cyclodehydration to the pyrylium cation. It was assumed that ring closure after dehydrogenation is possible via both pathway *a* [182] and pathway *b*:[183,184]



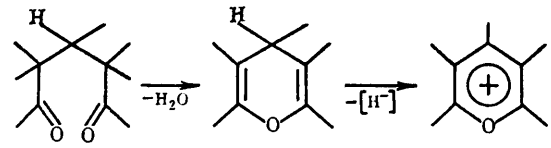
The study of the electrochemical oxidation potentials of saturated 1,5-diketones in acetonitrile using a rotating platinum electrode also led the authors[185] to the hypothesis of the initial formation of pentene-1,5-diones:



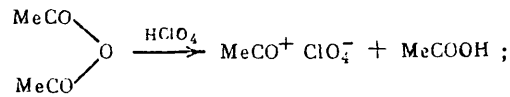
The overall process is

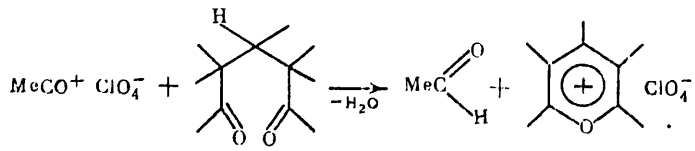


According to the second hypothesis, the initial stage in the formation of the pyrylium cation is the cyclodehydration of the 1,5-diketone with formation of a 4*H*-pyran, which is then converted into the pyrylium cation:



The abstraction of hydrogen was explained for a long time by the oxidising effect of the acid reagents. However, in the synthesis of pyrylium perchlorates in acetic anhydride, acetaldehyde was observed in the reaction mixture.[186] This finding permitted the hypothesis that organic carbonium ions, in particular that formed from acetyl perchlorate, may serve as hydride ion acceptors in salt formation†:





The supporters of the first hypothesis based their view on erroneous data showing that the cyclisation of 1,5-diketones to pyrans requires a strongly dehydrating medium[189] and also on the unsuccessful attempt to cyclise the saturated 1,5-diketone to a pyran with the aid of hydrobromic acid, which is a powerful protonating agent.[190] In the latter case one must bear in mind that the protonating medium promotes the reverse process involving the conversion of pyrans into diketones. Furthermore, there is no direct evidence for the formation of an unsaturated diketone from a saturated one and an indirect example illustrating the possibility of the dehydrogenation of an aliphatic straight chain by triphenylmethyl perchlorate is quoted in only one study,[189] the authors emphasing that it is unique.

On the other hand, it is fairly easy to split off water from a saturated 1,5-diketone with formation of 4*H*-pyrans; when carbonium ions are used, their dehydrating properties can be accounted for by the appearance of perchloric acid on interaction with acetic acid, in which most of the reactions are carried out:[191]

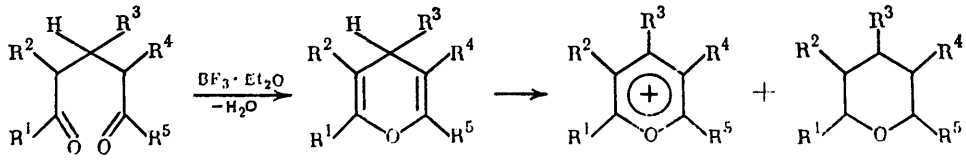
$$Ph_3CClO_4 + MeCOOH \rightarrow Ph_3COCOMe + HClO_4 .$$

Pyrylium salts have been synthesised[192] from a series of pentane-1,5-diones using trityl and acetyl cations in acetic anhydride, acetic acid, as well as their mixtures (in various proportions). It was shown that the joint action of trityl and acetyl cations is more effective than the action of each separately. On the basis of these experiments, it has been suggested that the pentanedione initially cyclises to a pyran, which is then dehydrogenated by triphenylmethyl perchlorate.

Concrete experimental evidence for the conversion of saturated 1,5-diketones into pyrylium salts via the formation of 4*H*-pyrans has been obtained recently. Thus, when penta-1,5-diones are treated with boron trifluoride etherate, 4*H*-pyrans are formed initially, their disproportionation subsequently resulting in the formation of pyrylium salts and tetrahydropyrans:[149]

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†The study of spectroscopic and solubility data for acyl perchlorates obtained from $AgClO_4$ and acid chlorides supports a covalent structure of the acetyl perchlorate $MeC(O)OClO_3$.[188]

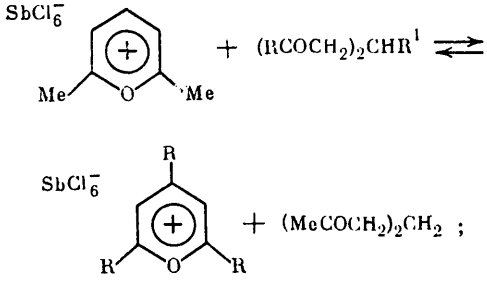


Boron trifluoride etherate apparently acts as a dehydrating agent in the first stage. This property of the trifluoride is well known.[193]

In addition, 3-carbaboranylpentane-1,5-diones are converted into 4*H*-pyrans in acetic anhydride, which acts as a dehydrating agent at room temperature.[119,178,179]

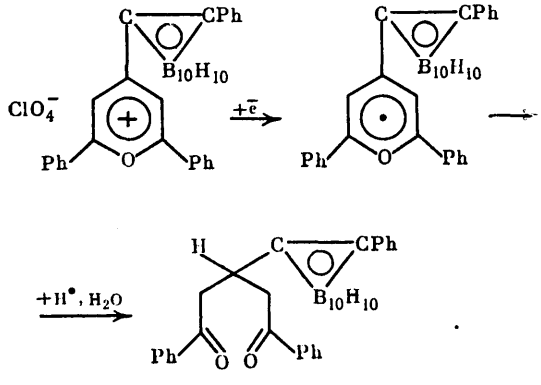
The above facts apparently make it possible to give preference to the formation of pyrylium salts from saturated 1,5-diketones via the 4*H*-pyran formation stage, as was done by a number of workers,[149,181,192,194] although it is so far difficult to give an unambiguous answer concerning the given mechanism, because the initial saturated 1,5-diketones themselves have different structures and the reaction media and the reagents employed are also varied.

Pyrylium salts can be converted in their turn into saturated 1,5-diketones. It has been shown[195] that the transfer of a hydride ion from the diketone to a less stable salt leads to the formation of a more stable salt and a new saturated 1,5-diketone:

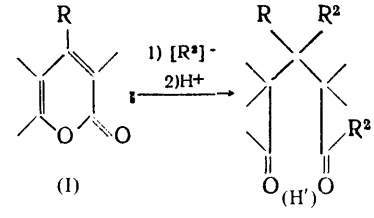


$R = R^1 = Ph$; $R = Ph$, $R^1 = H$.

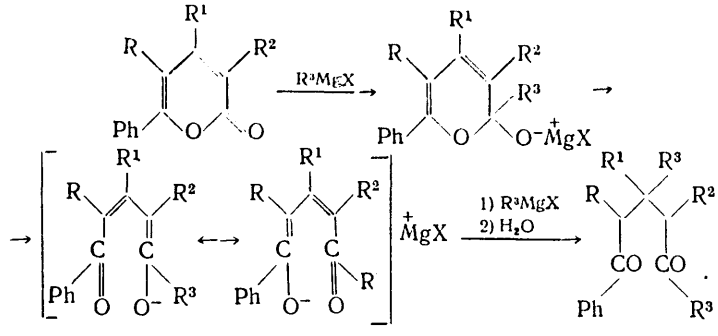
Pentene-1,5-diones are apparently formed from carbaboranylpyrylium salts via the stage in which a carbaboranylpyranyl radical is produced:[117,118]



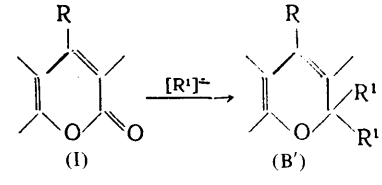
VIII. α-PYRONES–SATURATED 1,5-DIKETONES



When 2-pyrones (I)# are acted upon by Grignard reagents,[198–201] saturated 1,5-diketones (H′) may be formed. The interaction of phenylmagnesium bromide with α-pyrones containing the phenyl group in the 6-position, namely 6-phenyl-α-pyrone, 5-methyl-6-methyl-α-pyrone, and 3-methyl-6-phenyl-α-pyrone, leads exclusively to the formation of the corresponding pentane-1,5-diones in satisfactory yields.[199] In other cases saturated 1,5-diketones are formed together with keols, dienones, 2*H*-pyrans, etc. The reaction takes place via the following scheme:[199]

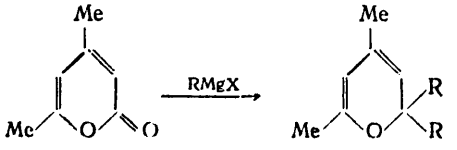


IX. α-PYRONES–2*H*-PYRANS

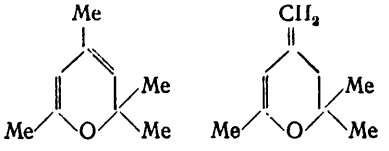


#Information about the methods of synthesis and properties of α-pyrones can be found in other reviews.[196,197]

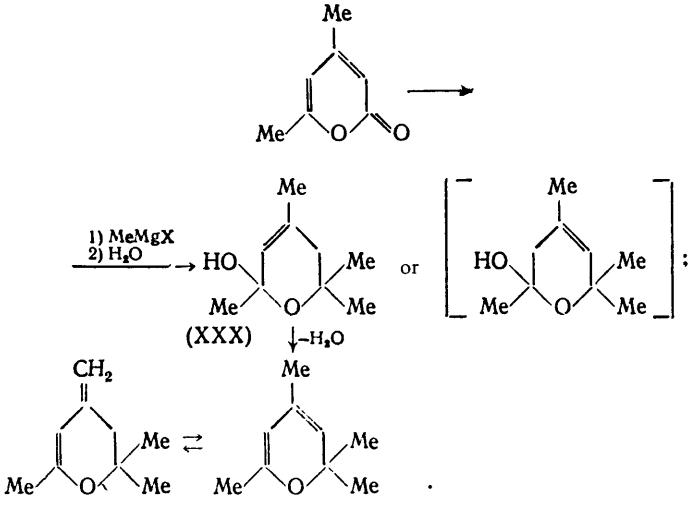
Treatment of α-pyrones with Grignard reagents is one of the main methods of synthesis of 2*H*-pyrans§.[32] The synthesis of 2*H*-pyrans by treating 2,4-dimethyl-α-pyrone with organomagnesium compounds was first reported by Gompper and Christmann:[202 203]



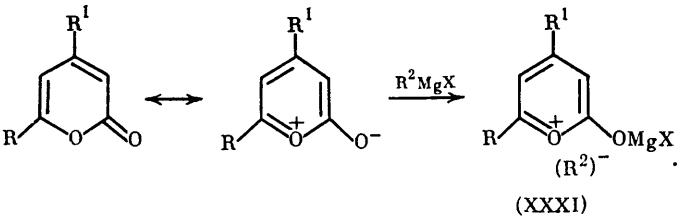
Repetition of this synthesis[204–210] showed that in the reaction involving methylmagnesium iodide, the products contained two isomers:



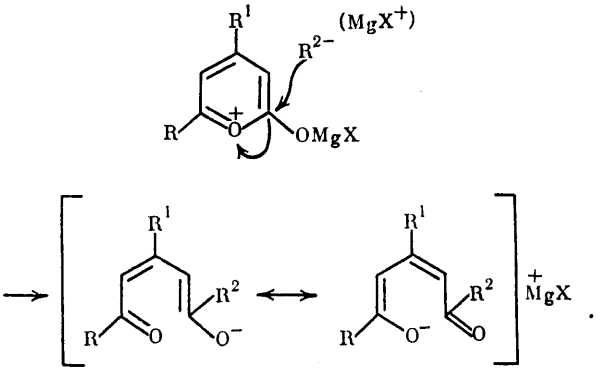
The isolation of the fairly unstable 6-hydroxy-2,2,4,6-tetramethyl-3,6-dihydro-2*H*-pyran (XXX) as an intermediate suggested the following mechanism of the above reaction:



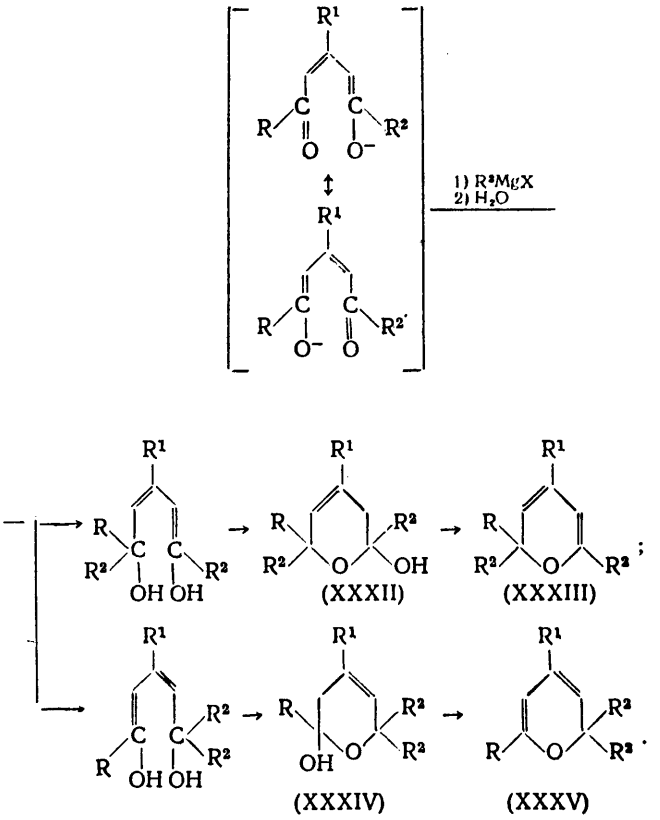
It is striking that, in the formation of 2*H*-pyrans by the reaction of α-pyrones with Grignard reagents, it is necessary to use a threefold excess [of the Grignard reagent], although it would appear that a twofold excess would have been sufficient according to the reaction stoichiometry. Experimental data showed that a complex of the pyrone with the Grignard reagent of type (XXXI) is formed initially¶:



On reaction with a second molecule of the alkylmagnesium halide, the ring opens with formation of the mesomeric enolate ion:



Finally, the enolate ion is attacked by a third molecule of the organomagnesium compound, which leads to two different 2*H*-pyrans—(XXXIII) and (XXXV):

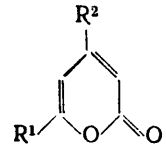


§ The 2*H*-pyrans (B′) are capable of valence isomerisation to the *cis*-dienones (C′).

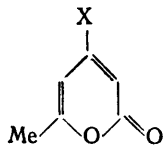
¶ The complex is a coloured compound, insoluble in ether, which decomposes during hydrolysis, occurring slowly even in an acid medium, with liberation of the initial α-pyrone.

It is striking that the dihydropyranols (XXXI) and (XXXIV) can be isolated only after hydrolysis in a neutral medium. After acid hydrolysis, the 2*H*-pyrans (XXXIII) and (XXXV) are formed.

The products of the interaction of the α-pyrones (XXXVI) and (XXXVII) with alkylmagnesium halides are 2*H*-pyrans as well as acyclic compounds: dienals, dienones, and saturated 1,5-diketones:[198]

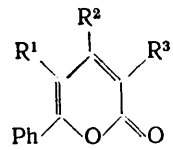


(XXXVI)
$R^1=R^2=H$; $R^1=H$, $R^2=Me$; $R^1=Me$, $R^2=Et$



(XXXVII)
X=OH, Cl, OMe .

The interaction of alkylmagnesium halides with α-pyrones (XXXVIII) containing the phenyl group in the 6-position has been investigated:[199]

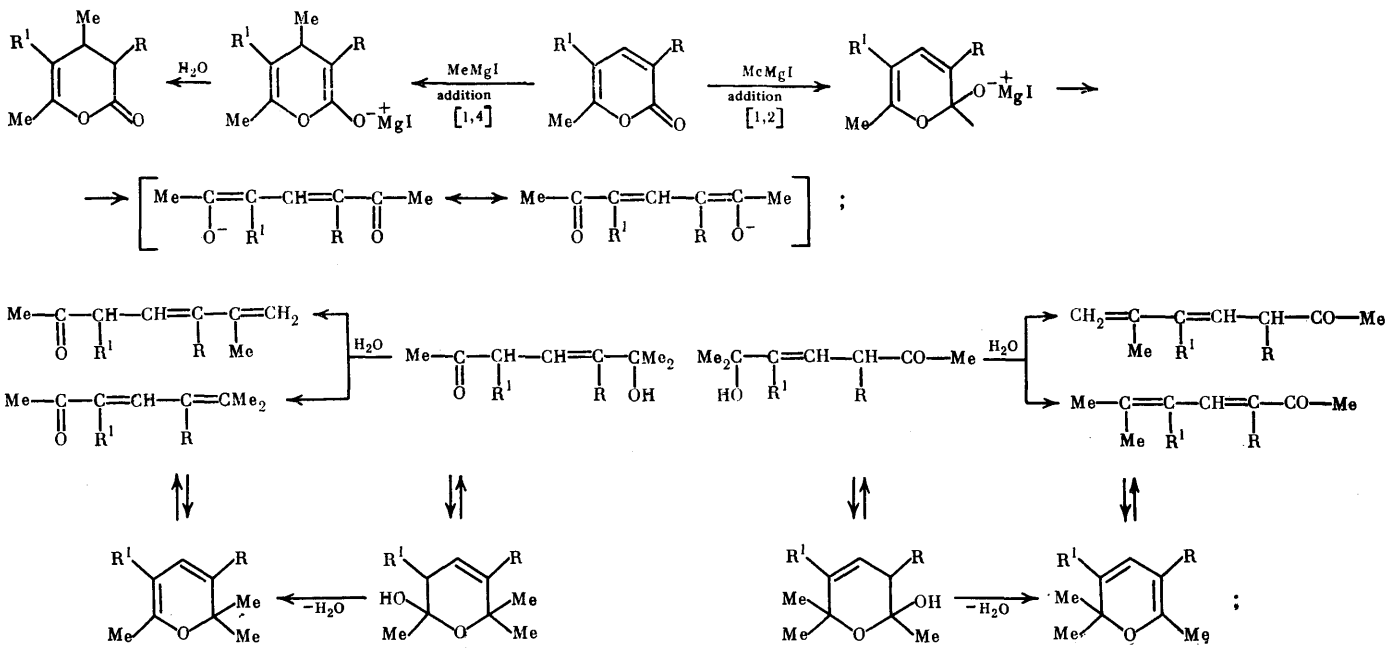


(XXXVIII)
$R^1=R^2=R^3=H$; $R^1=Me$, $R^2=R^3=H$; $R^1=R^3=H$, $R^2=Me$; $R^1=R^2=H$, $R^3=Me$; $R^1=R^3=H$, $R^2=Ph$.

Depending on the structure of the initial pyrone (XXXVIII), ketoenols, dienones, saturated 1,5-diketones, and dehydropyranols can be detected among the reaction products.

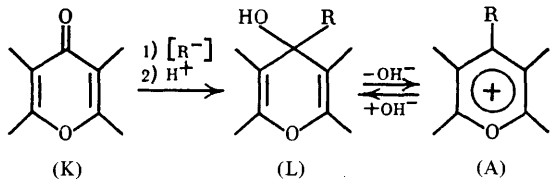
The study of the interaction of methylmagnesium iodide with α-pyrones unsubstituted in the 4-position[201,211] showed that 2*H*-pyrans can be obtained only from 3,5,6-trisubstituted derivatives. The 5,6-disubstituted α-pyrones give rise exclusively to compounds with a linear structure:

Scheme 2



R=R¹=Me; R=Ph, R¹=Me; R=H, R¹=Me; R=Me, R¹=H; R=H, R¹= *iso*-Pr; R=Ph, R¹=H; R=R¹=H

X. γ-PYRONES–γ-PYRANOLS–PYRYLIUM SALTS



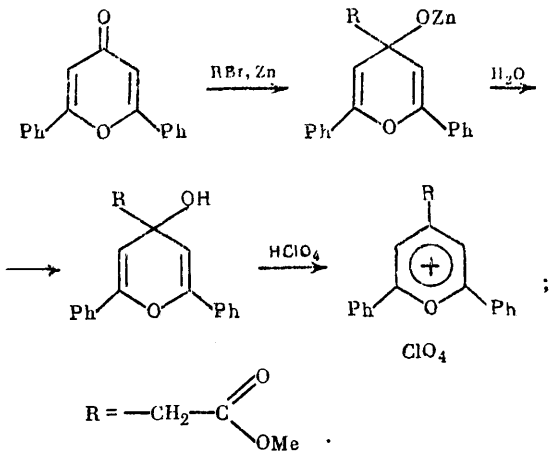
(K) (L) (A)

The γ-pyrones (K) are converted fairly readily into the γ-pyranols (L) and the latter are converted into pyrylium salts (A). The readily available 2,6-diphenyl- and 2,6-dialkyl-γ-pyrones therefore constitute a basis for the synthesis of a wide variety of pyrylium salts by interaction with organometallic compounds.

Thus the interactions of 2,6-dimethyl-γ-pyrones with methylmagnesium iodide and phenylmagnesium bromide yield respectively 2,4,6-trimethylpyrylium and 2,6-dimethyl-4-phenylpyrylium salts,[212] although Gomberg and Cone[213] and Elkaschef and Nossier[214] failed to observe a reaction between 2,6-dimethyl-γ-pyrone and phenylmagnesium bromide. There exist also other examples of the synthesis of pyrylium salts from γ-pyrones and organometallic compounds.[24,215,216]

It was assumed for a long time that the isolation of the intermediate γ-pyranols is impossible, although analogous compounds are known in the chromylium (benzopyrylium) and xanthylium series. It has been shown[109] that the alkoxides formed as a result of the interaction of γ-pyrones with organometallic compounds can be hydrolysed to γ-pyranols, which can be subsequently converted into pyrylium salts.

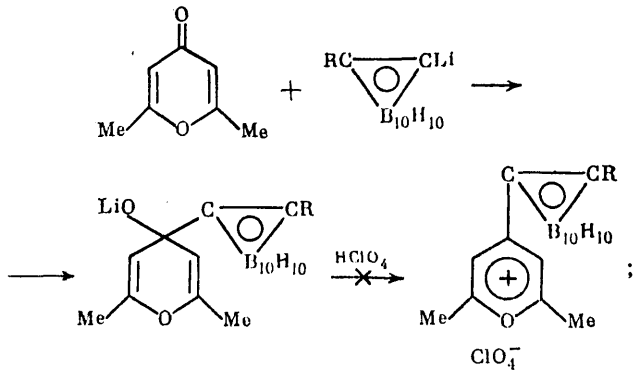
In recent years the range of organometallic compounds used in this reaction has been explained. For example, lithio-derivatives of the following heterocycles have been used: benzothiazole, pyridine, thiophen, and substituted furans.[108,109] 2,6-Diphenyl-γ-pyrone has been introduced into the Reformatskii reaction with formation of the methoxy-carbonylpyrylium cation:[217]



However, the authors were unable to extend this reaction to 2,6-dimethyl-γ-pyrone.

Indeed the reaction of γ-pyrones with organometallic compounds does not always proceed unambiguously. In particular, it has been noted[214] that the hydrolysis of the reaction mixture with dilute perchloric acid yields the pseudo-base and not the pyrylium salt.

After the interaction of 2,6-dimethyl-γ-pyrone with lithio-derivatives of *o*-carbaboranes, it was possible to isolate the intermediate lithium alkoxides derived from 2,6-dimethyl-4-R-*o*-carbaboranyl-γ-pyranols, which are precipitated during the reaction.[116,119] They are fairly stable high-melting point powders, although the alkoxides of tertiary carbaborane alcohols are usually unstable.[218] It was not possible to convert the alkoxides into the carbaboranyl-γ-pyranols on treatment with water or into pyrylium salts on treatment with perchloric acid:



R = H, Me, Ph.

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Another specific feature of six-membered oxygen-containing heterocycles, namely the tendency towards ring opening, has been strikingly manifested against the background of the intense investigations of the recyclisation of the heterocyclic systems.[11–14] The competition between two reaction pathways—recyclisation and ring opening—actually determines the character of the reactivity of these compounds.

The experimental and theoretical data accumulated hitherto enabled us to put forward a general mechanism for the reactions of six-membered oxygen-containing heterocycles (pyrylium salts, pyrans, and pyrones) and their open-chain forms, which, in our view, may be of definite assistance to synthetic chemists in selecting the method of synthesis of compounds belonging to the above classes or in the analysis of the structure of the substances formed in the course of the reactions indicated above. The data surveyed in this review are extremely useful for the elucidation of the following important problems in the chemistry of six-membered oxygen-containing heterocycles: the mechanism of the dehydroaromatisation of 4*H*-pyrans and the valence tautomerism of 2*H*-pyrans, the mode of reaction of α- and γ-pyrones with organometallic compounds, the structure of the pseudobases of pyrylium salts and the conditions governing their formation, the pathways leading to the conversion of saturated 1,5-diketones into pyrylium salts, etc. The series of studies by Katritzky and co-workers,[219–223] who investigated the kinetics of the opening of the rings of water-soluble

pyrylium salts in hydrolysis over a wide pH range and in ammonolysis by amines and who demonstrated the structure of the products by ^{1}H and ^{13}C NMR, is instructive in connection with the foregoing findings.

Questions concerning the opening of the pyran, pyrone, and pyrylium rings as a result of their coordination interaction with metal salts are of considerable interest. It is known that, in the complex of the 2*H*-pyran system with tungsten carbonyl, the ligand is fixed in the open-chain diene form;[224] this is not unexpected bearing in mind the high stability of this isomer in the non-coordinated state.[42,225] At the same time the formation of π-allyl complexes and the fixation of the open-chain forms of the ligands in the complexes of pyrylium salts with palladium(II) [226-229] and copper[230] indicate the possibility of using complex formation as an effective method for the opening of the rings in six-membered heterocycles and for the stabilisation, on coordination, of the isomers which are unusual for the free heterocycles.

Finally, we emphasise that the experimental and theoretical development of questions concerning the relative stabilities of the valence tautomers of oxygen-containing heterocycles makes it possible to identify the characteristic features of the steric and electronic structures which control the photochemical reactivity of the series of heterocyclic systems examined above[81,83,231] and assists in the search for the specific synthesis of photochromic systems with a specified set of properties.

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