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OXYGEN-CONTAINING HETEROCYCLIC COMPOUNDS FROM 1,5-DIKETONES. (REVIEW)

V. G. Kharchenko, N. V. Pchelintseva, L. I. Markova, and O. V. Fedotova

Literature and characteristic experimental data correlated in the review concern the intramolecular cyclization by various means of substituted 1,5-diketones of the acyclic, semi-, and bicyclic series, proceeding to the formation of oxygen-containing heterocycles, such as pyrans, pyrylium salts, di- and tetrahydrofurans, and their condensed analogs, aroylfurans etc.

Keywords: synthesis, structure, properties, 1,5-diketones, pentane-1,5-diones, 2-pentene-1,5-diones, 1,3,5-triaryl-2,4-dichloro-2-pentene-1,5-diones, arylidenedicyclanones, heterylidenedicyclanones, 2-(3-oxo-1,3-diphenylpropyl)tetralones, 4-(1,3-diaryl-3-oxopropyl)pyrazolones, pyrans, dihydropyrans, tetrahydropyrans, *sym*-octahydroxanthenes, pyrylium salts, aroylfurans, 2-aroyl-4-chlorofurans.

Diketones, the carbonyl groups of which are separated by a chain of three carbon atoms (1,5-diketones), are distinguished by the ability to undergo intramolecular heterocyclization under the action of acids, and also on ionic and catalytic hydrogenation, forming compounds containing six-membered (occasionally also five-membered) oxygen-containing rings.

Numerous procedures for obtaining 1,5-diketones have been developed up to the present time [1]. Their hetero- and carbocyclization, their nucleophilic, electrophilic, and other reactions have been studied. This opens broad possibilities for obtaining from them both carbo- and heterocyclic compounds, which are of interest in the synthesis of biologically active, pharmaceutical preparations, pesticides, vitamins, steroids, dyestuffs, and other substances having a practical use.

1. HETEROCYCLIZATION OF 1,5-DIKETONES BY THE ACTION OF ACIDS

Heterocyclization of 1,5-diketones occurs particularly readily under the action of such acids as $HClO_4$, HHal, H_2SO_4, H_3PO_4, $FeCl_3$, $SbCl_5$, $BF_3{\cdot}OEt_2$, etc. with the formation of pyrans, pyrylium salts or mixtures of them with di- or tetrahydropyrans.

1.1. Formation of Pyrans and Their Condensed Analogs

1,5-Diketones containing electron-withdrawing groups in positions 1 and 5 or *gem*-substituted in position 3 form 4H-pyrans under the action of acids. Compounds of type **1** were first synthesized by the heterocyclization of 1.5-biscarboxypentane-1,5-diones by the action of sulfuric acid [2].

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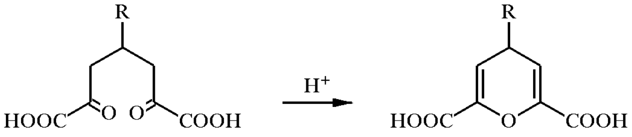
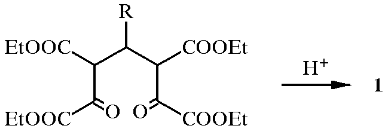


1

R = H, Me, Et

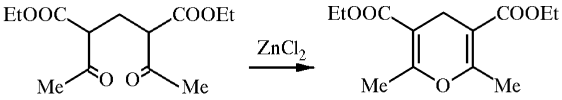
The products **1** (R = H, Me) were also obtained by the action on 1,2,4,5-tetracarbethoxy-3R-pentane-1,5-diones of first dilute and then concentrated sulfuric acid [3].



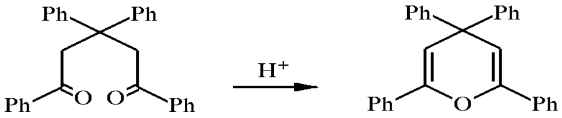
R = H, Me

Under these conditions hydrolysis and decarboxylation of the carbethoxy groups in the positions β to the keto groups occur with subsequent heterocyclization.

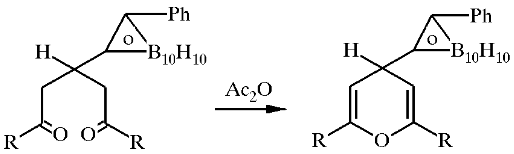
As a rule 1,5-diketones containing a methyl or methylene group as well as a C=O group form carbocyclization products under the action of acids. However it turned out that 3,5-dicarbethoxy-2,6-heptanedione is converted into 3,5-dicarbethoxy-2,6-dimethyl-4H-pyran in the presence of zinc chloride in a mixture of acetic acid and its anhydride [4].



The stable tetraphenyl substituted 4H-pyran (R = R^1 = Ph) is formed by the action of phosphoric anhydride on 1,3,3,5-tetraphenylpentane-1,5-dione [5,6].



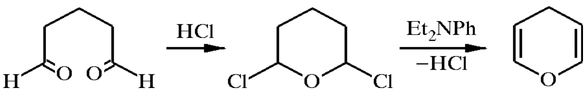
The facile heterocyclization of 1,5-diketones containing a carborane substituent into 4H-pyran **2** under mild conditions, *viz*. the action of acetic anhydride, has been reported [7].



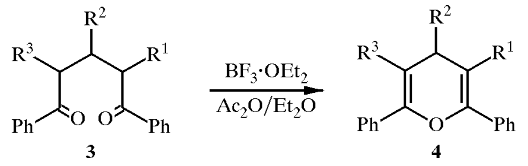
2

R = *t*-Bu, Ph

4H-Pyrans are compounds of low stability, however the simplest of them was successfully obtained by the action of hydrogen chloride on glutaric aldehyde (-10 to -15°C) and subsequent heating of the reaction mixture in vacuum in the presence of diethylaniline [8].



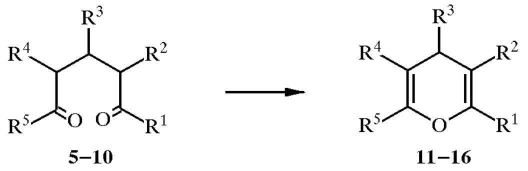
Alkyl- and aryl-substituted 1,5-diketones are usually converted rapidly into pyrylium salts by the action of acids. A systematic study of the heterocyclization of such diketones enabled conditions to be found limiting the reaction to the formation of 4H-pyrans. For example the action of a mixture of boron trifluoride etherate and acetic anhydride on diketones **3** in diethyl ether gave the 4H-pyrans **4** and not the pyrylium salt [9,10].



3, 4 $R^1 = R^3 = H$, R^2 = Ph, *p*-$MeOC_6H_4$, *o*-ClC_6H_4, furyl-2, R^1 = Me, R^2 = Ph, R^3 = H

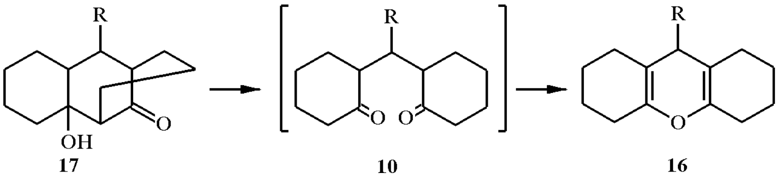
The yields of product were 70-90%, and there were no traces of 2H-pyrans.

Condensed systems containing a 4H-pyran ring **11-16** were obtained on heterocyclization of semi- and bicyclic 1,5-diketones **5-10** under analogous conditions [8,9,11,12].



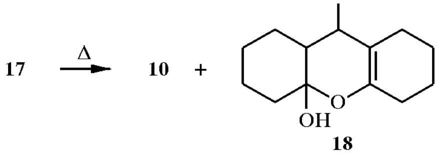
5, 11 R^1 = Ph, R^2 = H, $R^3 = (MeO)_2C_6H_3$, R^4+R^5 = *o*-$C_6H_4(CH_2)_2$; **6, 12** $R^1 = R^3$ = Ph, R^2 = H, $R^4+R^5 = (CH_2)_3$; **7, 13** $R^1 = R^3$ =Ph, R^2 = H, $R^4+R^5 = (CH_2)_4$; **8, 14** $R^1+R^2 = R^4+R^5 = (CH_2)_3$, R^3 = H; **9, 15** $R^1+R^2 = (CH_2)_4$, R^3 =H. $R^4+R^5 = (CH_2)_3$;**10, 16** $R^1+R^2 = R^4+R^5 = (CH_2)_4$, R^3 = H, Me, *n*-Pr, Ph, *p*-$MeOC_6H_4$

On heating the tricyclic ketols **17**, which are products of the intramolecular aldol condensation of arylidene- and heterylidenecyclanones, in a mixture of Ac_2O–AcOH (1 : 1) condensed tricyclic products, the *sym*-(octahydro-9H-xanthenes) **16**, are formed [9,10].

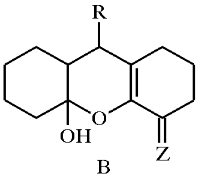


10, **16**, **17** R = *p*-$Me_2NC_6H_4$, *p*-ClC_6H_4, *o*-FC_6H_4, *p*-BrC_6H_4, 2-furyl, 4-methylfur-2-yl, 2-thienyl

On melting ketols **17** (R = 2-furyl, Ph, *p*-$MeOC_6H_4$), a mixture is obtained of the corresponding 1,5-diketones **10** and hemiacetals **18**, and when R = Ph or *p*-$MeOC_6H_4$ both forms were successfully isolated [13-15].



The diketones **10** (R = Ph, 2-furyl) are partially (10-20%) converted in solution to the corresponding hemiacetals **18,** which indicates the ring–chain isomerization of diketone (A) ⇌ hemiacetal (B), which has been studied in more detail using δ-dicyclanones [13-16]. The most clear A ⇌ B transition was observed when both rings in the δ-dicyclanone molecule are six-membered. Replacement of only one of them by a five-membered significantly reduces the content of cyclohemiacetal B in the equilibrium mixture or this form is absent. The presence of an ylidene substituent (Z) or a carbonyl group in the position α to one of the carbonyl groups of diketones **10** leads to them existing only in form B [13,14].

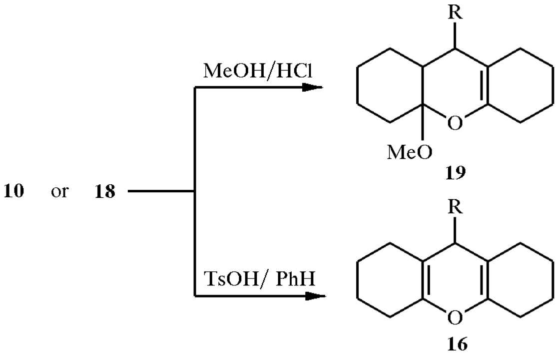


B

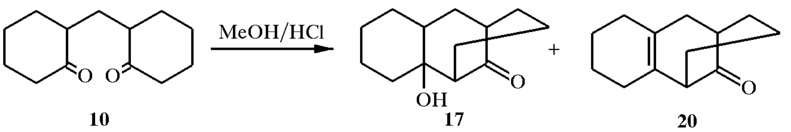
Z = O, PhCH, *p*-MeC$_6$H$_4$, (2-furyl)-CH

The simplest representative of compounds **10,** methylenedicyclohexanone, is found in solution and in the crystalline state only in the diketone form A.

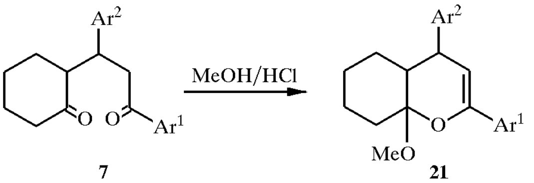
Bicyclic diketones enter into the same reactions as the hemiacetals. The action of hydrogen chloride in methanol on diketones **10** (R = Ph, *p*-MeOC$_6$H$_4$, 2-furyl) and their hemiacetals **18** gave the corresponding acetals **19** and *sym*-octahydroxanthene **16** on reacting compounds **10** or **18** (R = Ph, *p*-MeOC$_6$H$_4$) with tosic acid in benzene [13-16].



When R = H diketone **10** is converted under the action of hydrogen chloride in methanol into the unsubstituted β-diketol **17** and its dehydration product **20**, but not the acetal **19** [13].

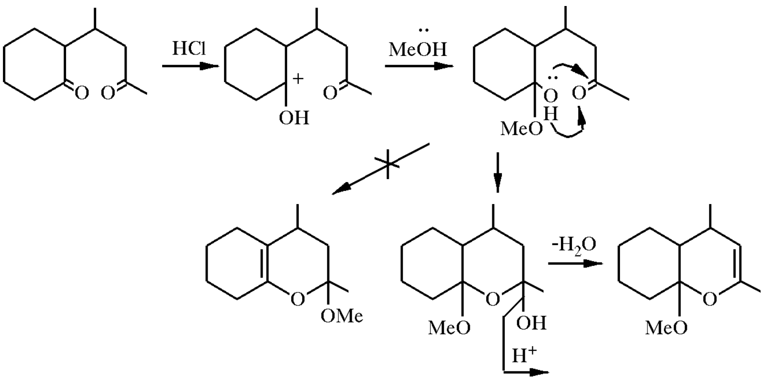


Exclusively acetals **21** are readily formed from semicyclic 1,5-diketones of type **7** in methanol under the action of hydrogen chloride or sulfuric acid [16,17].

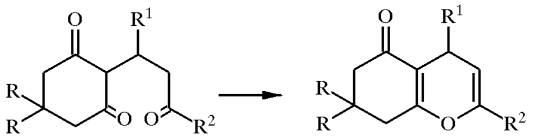


Even under the action of hydrogen sulfide under the given conditions on diketone **7** ($Ar^1 = Ar^2 = Ph$) the corresponding acetal of type **21** is formed and not the thioacetal [18], which indicates the high rate of cyclization onto oxygen.

According to [16] a methoxy group must occupy position 2 in the acetal **21**, however it was shown later that it was located on the $C_{(9)}$ atom [17]. The reaction mechanism may be represented by the following scheme.



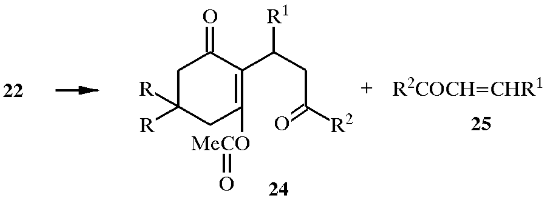
The semicyclic oxo-1,5-diketones **22** undergo heterocyclization on boiling with acetic anhydride [19-22] or in acetic acid with a few drops of added sulfuric acid [22], and also on heating with TsOH in toluene [19-22], forming the stable 5-oxo-5,6,7,8-tetrahydrochromenes **23** in 71-93% yield.



22 **23**

22, **23** R = H, R^1 = H, R^2 = Me, $R^1 = R^2$ = Ph, R^1 = *p*-$MeOC_6H_4$, R^2 = Ph, $R^1 = R^2$ = *p*-$MeOC_6H_4$; R = Me, $R^1 = R^2$ = Ph

The effect of reaction temperature and the nature of the substituents shows in the character of the conversion of triketones **22**. Boiling triketones **22** (R = H, Me, $R^1 = R^2$ = Ph; R = Me, R^1 = *p*-$MeOC_6H_4$, R^2 = Ph) in acetic anhydride leads to the corresponding oxohydrochromene **23**, but at temperatures below 130°C the resulting products of acylation of the enol form **24** undergo retro-Michael-addition, as a result of which mixtures of compound **24** and the α,β-unsaturated ketone **25** were obtained [23,24].

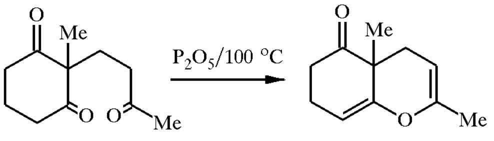


22, **24**, **25** R = H, $R^1 = R^2$ = Ph; R = Me, R^1 = Ph, *p*-$MeOC_6H_4$, R^2 = Ph

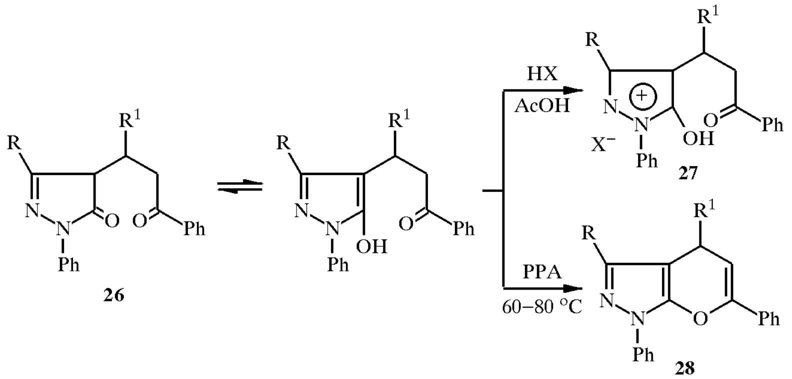
For example, a mixture of ~20% enol acetate **24** and ~63% 4-methoxybenzylideneacetophenone is formed on boiling oxo-1,5-diketone **22** (R = Me, R^1 = *p*-$MeOC_6H_4$, R^2 = Ph) in acetic acid or acetic anhydride [23,24].

On heating triketone **22** ($R = R^1$ = H, R^2 = *p* -$MeOC_6H_4$) with acetic anhydride in the presence of sodium acetate, the corresponding enol acetate **24** is formed [25].

2,10-Dimethyl-5-oxo-5,6,7,10-tetrahydro-$\Delta^{8,9}$-chromene was obtained by heating 2-methyl-2-(3-oxobutyl)dihydroresorcinol with phosphorus pentoxide [20].



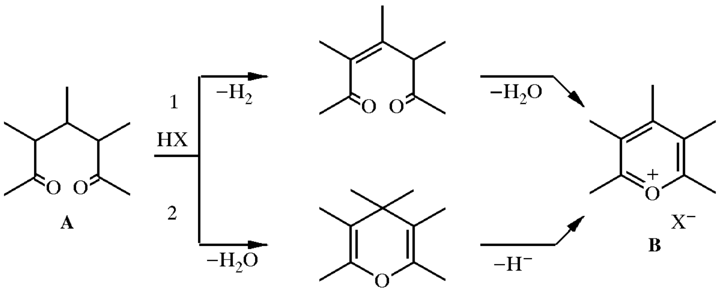
The semicyclic 1,5-diketones **26**, obtained from 3-methyl-1-phenyl- and 1,3-diphenylpyrazol-5-ones [1], under the action of protic acids (HCl, $HClO_4$, HBF_4) do not form 4H-pyranopyrazoles but are converted into the 5-hydroxy-4-(oxopropyl)pyrazolium salt **27**, and only on using a weakly protonating reagent such as polyphosphoric acid and heating (60-80°C) are the stable 4H-pyrano[3,2-d]pyrazoles **28** obtained [1,26,27].



26-**28** R = Me, R^1 = Ph, X = Cl, ClO_4; R = Me, R^1 = *m*-$O_2NC_6H_4$, X = ClO_4; R = R^1 = Ph, X = ClO_4;
26, **27** R = Me, R^1 = *p*-$MeOC_6H_4$, X = Cl, ClO_4, BF_4; **26**, **28** R = Ph, R^1 = *m*-$O_2NC_6H_4$

1.2. Preparation of Pyrylium Salts

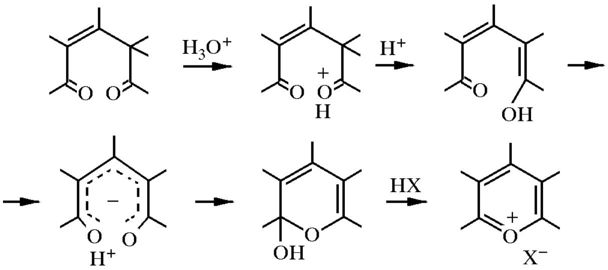
The most characteristic property of 1,5-diketones is the heterocyclization by the action of acids ($HClO_4$, HHal, H_3PO_4, $FeCl_3$, CF_3COOH, BF_3OEt_2, $SbCl_3$, etc.) leading to pyrylium salts and their condensed analogs. Numerous investigations have been devoted to the formation of such salts [9,11,17,28-40). Much attention has been paid to the mechanism of the reaction which includes dehydrogenation and dehydration. Two possible variants for the conversion of diketone A into salt B are considered: 1) the initial formation of unsaturated 1,5-diketone and its subsequent dehydration [41-45], 2) initial dehydration with the formation of a 4H-pyran and dehydration of the latter [11,28-30,38-40,46-48].



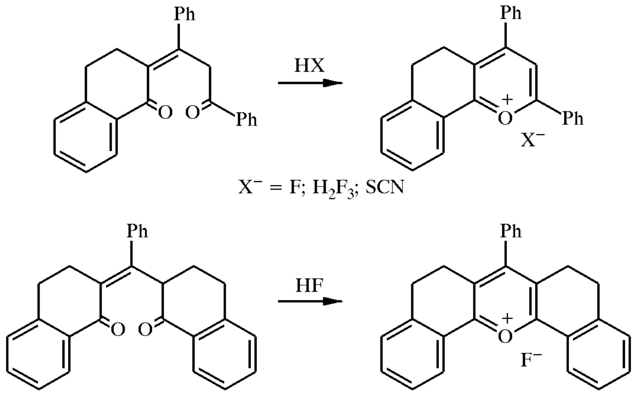
It has been proposed that the formation of pyrylium salt B according to the first variant is possible by both routes a [49] and b [41,45].

Support for the first variant is based on the instability of 4H-pyrans [50] and by the unsuccessful attempt to cyclize the saturated 1,5-diketones into the 4H-pyran by the action of hydrobromic acid, which leads to a pyrylium salt [43]. In reality, the unsaturated 1,5-diketone forms pyrylium salts exceptionally readily under the action of acids [51-58].

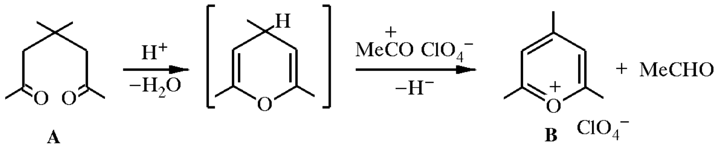
Kinetic investigations have enabled the following mechanism to be proposed for the heterocyclization of unsaturated 1,5-diketones [51,52,57,59].



A. R. Katritzky has used unsaturated 1,5-diketones for the synthesis of difficultly accessible pyrylium salts [54-58].

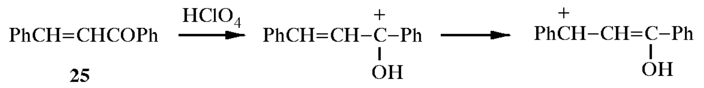


A second variant for the cyclization of 1,5-diketones into pyrylium salts by the action of acids was proposed by Dilthey [60-64], and then by Allen and coworkers [16,30]. It was suggested that 4H-pyrans are generated initially, but under the mild conditions readily form pyrylium salts [60-66] by the action of protic and aprotic acids. The fission of hydride ion was explained by the oxidizing action of the acids, and proved to be mistaken [16,60-62]. When obtaining pyrylium perchlorates in acetic anhydride, acetaldehyde was discovered in the reaction mixture [42,67] and this is the basis for the hypothesis that the acceptors of hydride ion are organic carbocations, particularly acetyl cation [42,67].

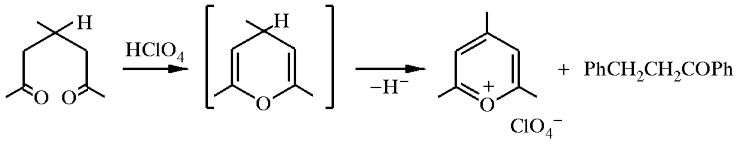


$$\left[(\mathrm{MeCO})_2\mathrm{O} \xrightarrow{\mathrm{HClO_4}} \overset{+}{\mathrm{MeCO}}\ \mathrm{ClO_4^-} + \mathrm{MeCHO}\right]$$

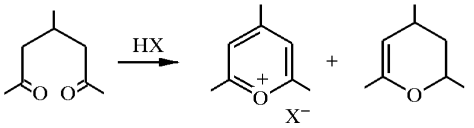
As a result reagents readily forming carbocations such as triphenylmethyl perchlorate, *tert*-butyl chloride, etc. [3,4,35,41,68,69] are used. On interaction with 1,5-diketones these act not only as hydride ion acceptors but also as donors of anion. Chalcones are also used in the role of hydride ion acceptors in the presence of acids [33,70-73]. By the action of perchloric acid [33] or boron trifluoride [70,71] the yield of pyrylium salt when chalcone **25** was present in the reaction mixture reached 95%, and in its absence less than 40% [33,71,73].



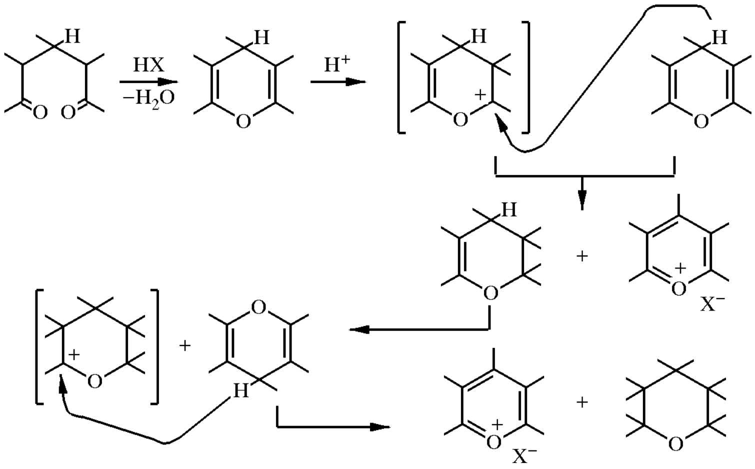
$$\underset{\mathbf{25}}{\mathrm{PhCH{=}CHCOPh}} \xrightarrow{\mathrm{HClO_4}} \mathrm{PhCH{=}CH{-}}\underset{\mathrm{OH}}{\overset{+}{\mathrm{C}}}\mathrm{{-}Ph} \longrightarrow \mathrm{Ph}\overset{+}{\mathrm{C}}\mathrm{H{-}CH{=}}\underset{\mathrm{OH}}{\mathrm{C}}\mathrm{{-}Ph}$$



It was suggested by A. T. Balaban [33] that disproportionation might take place in the action of acids on 1,5-diketones in the absence of a hydride ion acceptor with the formation of pyrylium salts and dihydropyrans.



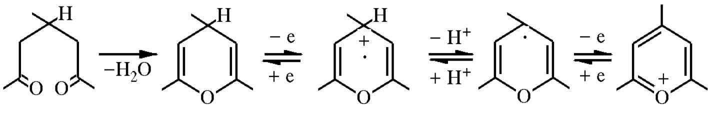
Systematic investigations of the reaction of 1,5-diketones with proton acids ($HClO_4$, CF_3COOH, HHal) and boron trifluoride etherate enabled it to be established that the 4H-pyrans and their condensed analogs formed initially may disproportionate to pyrylium salts and the corresponding tetrahydropyrans [9,17,38,40,74-78]. It is possible that the double bond in the 4H-pyran ring, as in the case of chalcones, is protonated by the acids with the formation of a carbocation which is also a hydride ion acceptor [39,77,79].



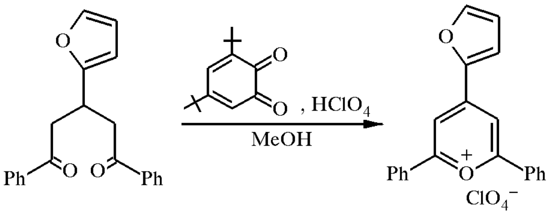
The disproportionation of pyrans has been confirmed experimentally [9,17,38,76,78,79]. The products of this conversion are formed most smoothly in the action on substituted pyrans, tetrahydrochromenes or *sym*-octahydroxanthenes of trifluoroacetic acid or boron trifluoride etherate in acetic acid [74-78]. In many cases the disproportionation is complicated by side reactions such as carbocyclization or further conversions [40,77].

Stable thiopyrans and their condensed analogs disproportionate under the action of acids, generally quantitatively [80].

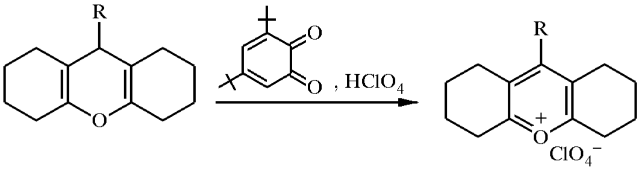
The transfer of hydride ion to a carbocation occurs mainly as a result of the stepwise transfer of electron–proton–electron [9,80], although in the case of other heterocycles the transfer of hydride ion may have a different character: electron–electron–proton, proton–electron–electron [81,82].



A preparative method of obtaining pyrylium salts from 1,5-diketones has been developed using 3,5-di-*tert*-butyl-*o*-benzoquinone and perchloric acid as oxidizing agent. The synthesis of the previously unavailable pyrylium salt containing a furyl substituent in position 4 was successfully effected in this way [9].



Since initially 1,5-diketones are heterocyclized into 4H-pyrans, the relationship of the latter towards 3,5-di-*tert*-butyl- and 3,4,5,6-tetrachloro-*o*-benzo-quinones was studied [9,10,83]. 9R-*sym*-Octahydro-xanthenes **16** form pyrylium perchlorates **29** in high yield (70-80%) with 3,5-di-*tert*-butyl-*o*-benzoquinone and perchloric acid in ether at a ratio of pyran : quinone : acid of 1 : 1.5 : 2.

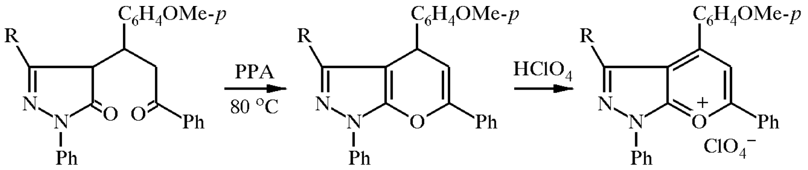


16 **29**

16, **29** R = H, *n*-Pr, *p*-$MeOC_6H_4$, *p*-ClC_6H_4, 2-fuyl

It turned out that the formation of a pyrylium cation also takes place in the absence of acid by the action of 3,4,5,6-tetrachloro-*o*-benzoquinone on pyrans. The authors concluded [9,83] that in the dehydrogenation of pyrans with *o*-benzoquinones two molecules of the latter participate, one of which accepts the electron and the other the proton. A probable mechanism for this unusual process was suggested [9].

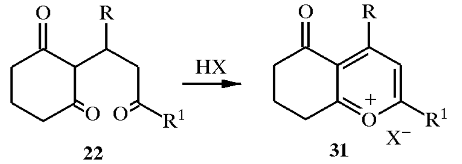
Only pyrylium salts are formed in the absence of hydride ion acceptors in dilute solutions of 1,5-diketones under the action of acids [78]. In this case the disproportionation process is suppressed due to the oxidizing action of atmospheric oxygen contained in the reaction mixture. The yield of the salts indicated is increased on bubbling oxygen. The ability of 1,5-diketones to heterocyclize with the formation of pyrylium salts under the action of acids is caused to a significant degree by the special features of their structure and the nature of substituents. 4-(1,3-Diaryl-3-oxopropyl)pyrazolones **26** form salts **30** under the action of PPA (80°C) and then perchloric acid only in the presence of electron-donating substituents in the 4-oxopropyl fragment [84].



26 **28** **30**

26, **28**, **30** R = Me, Ph

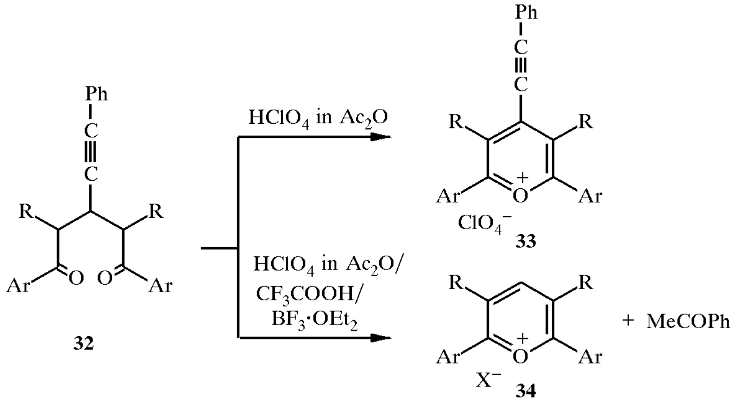
Similarly in the case of the semicyclic oxo-1,5-diketones of type **22**, the formation of salts **31** takes place only in the presence of *p*-methoxyphenyl substituents in the 4-oxopropyl fragment [85]. This is explained by the increase in electron density at position 4 of the generated pyran ring which enables its more facile oxidation to the pyrylium salt.



22 **31**

22, 31 R = p-$MeOC_6H_4$, R^1 = Ph, p-$MeOC_6H_4$, X = BF_4;
R = Ph, R^1 = p-$MeOC_6H_4$, X = BF_4, ClO_4

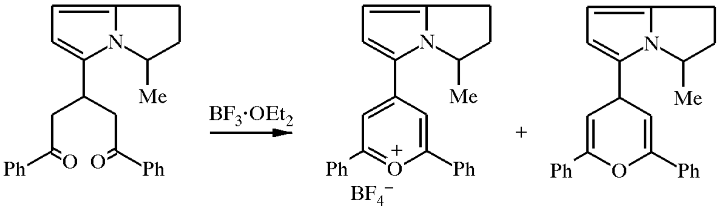
1,5-Diketones **32** containing a phenylethynyl substituent in position 3, depending on the conditions, form ethynyl-substituted pyrylium salts **33** or undergo conversion into γ-unsubstituted pyrylium salts **34** under the action of acids and boron trifluoride etherate. The triple bond is seemingly hydrated under the reaction conditions with the formation of a carbonyl group [86].



32 **33** **34**

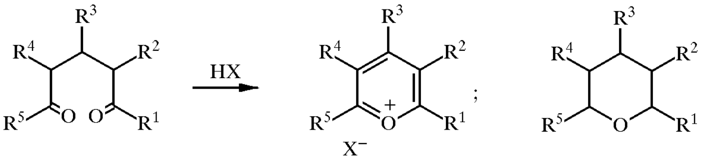
32–34 R = H, Ar = Ph, p-$MeOC_6H_4$; R = Me, Ar = Ph,
34 X = ClO_4, CF_3COO, BF_4

Boron trifluoride etherate proved to have an effective cyclizing action on 1,5-diketones. In methanol 3-(3-methyl-1,2-dihydro-5-pyrrolizinyl)-1,5-diphenyl-1,5-pentanedione is converted into the pyrylium tetrafluoroborate **35** and the corresponding pyran **36** [87].



35 **36**

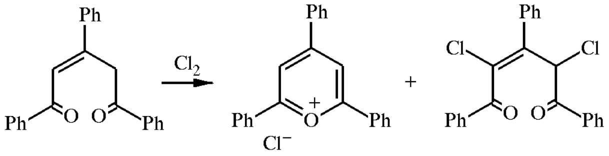
It was noted in [88] that the action of hydrogen bromide on 1,5-diketones did not effect heterocyclization. However a systematic study of the reaction of diketones of types **3, 6,** 7, and **10** with hydrogen halides (HCl, HBr, HI) showed that in anhydrous acetic acid or mixtures of it with absolute ether the corresponding pyrylium halides **37-40** were formed, and in several cases mixtures of them with tetrahydropyrans **41** and **42** [38,75,89,90], indicating disproportionation of the initially generated 4H-pyrans.



3, 6, 7, 10 **37–40** **41, 42**

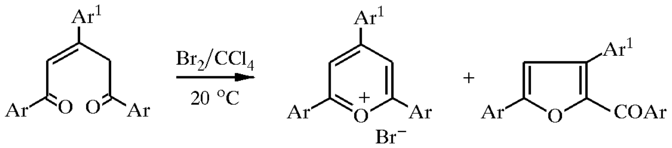
3, 37, 41 $R^1 = R^5$ = Ph, R^2 = H, Me, R^3 = Me, H, R^4 = H, X = Br; $R^1 = R^3 = R^5$ = Ph, R^4 = H,
R^2 = H, X = Br, R^2 = Me, X = Cl, Br; **6, 38** R^1 = Ph, R^2 = H, R^3 = H, Ph, $R^4+R^5 = (CH_2)_3$,
X = Cl; **7, 39** R^1 = Ph, $R^2 = R^4$ = H, $R^4+R^5 = (CH_2)_4$, X = Cl; **10, 40, 42** $R^1+R^2 = R^4+R^5 = (CH_2)_4$,
R^3 = H, Me, X = Br, Cl

It was shown in several examples that pyrylium halides are also formed by the action of bromine or iodine on 1,5-diketones [88,89,91], although chloro-substituted 1,5-diketones are obtained by the action of chlorine [89-92]. The readily heterocyclizing unsaturated 1,5-diketones are the exception. Diketone **43** forms pyrylium chloride **37** (50% yield) and 1,3,5-triphenyl-2,4-dichloro-2-pentene-1,5-dione (37% yield) on reaction with chlorine under mild conditions (20°C, CCl_4) [93].



43 **37** **44**

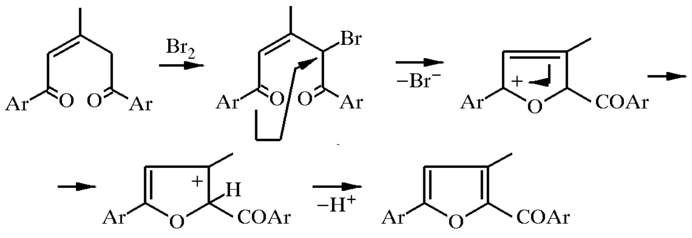
The reaction of bromine on unsaturated 1,5-diketones of type **43** [93,94], depending on the character of the substituent, forms aroylfurans **45** in addition to the pyrylium bromides **37**, or in the case of the triphenyl-substituted diketone **43**, 4-bromo-1,3,5-triphenyl-2-pentene-1,5-dione is formed.



43 **37** **45**

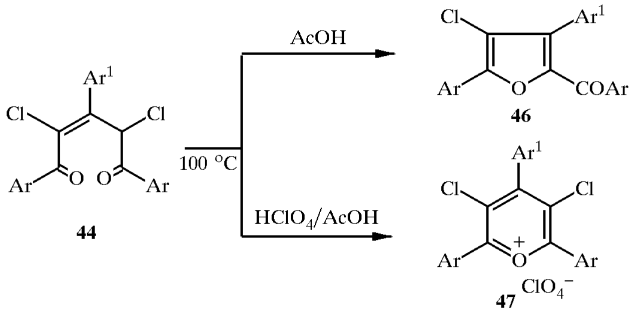
37, 43, 45 Ar = Ph, Ar^1 = *p*-ClC_6H_4; Ar = *p*-ClC_6H_4, Ar^1 = Ph

The mechanism of formation of aroylfurans **45** may be represented by the following scheme.



It must be noted that unsaturated 1,5-diketones are heterocyclized by the action of bromine at 20°C and substituted saturated pentane-1,5-diones form pyrylium bromides at 118°C (in glacial acetic acid) [88,89,91].

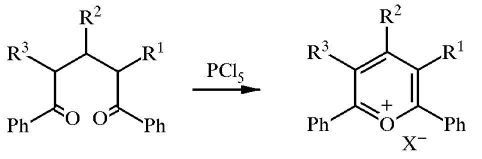
Unlike the unsaturated triaryl-substituted 1,5-diketones **43**, it is necessary to heat the reaction mixture to 100°C for the cyclization of their 2,4-dichloro derivatives **44**, but the direction of the conversion depends on the acidity of the medium [93]. On heating in acetic acid 4-chlorofurans **46** are formed (~90% yield), but the action of perchloric acid in acetic acid forms 3,5-dichloro-2,4,6-triarylpyrylium perchlorates (42-44% yield) [93].



44–47 Ar = Ar^1 = Ph; Ar = Ph, Ar^1 = *p*-ClC_6H_4; Ar = *p*-ClC_6H_4, Ar^1 = Ph

On carrying out the reaction of dichloroketones **44** with perchloric acid in a mixture of acetic acid and acetic anhydride the yields of perchlorates **47** grew to 77%.

The reaction of substituted pentane-1,5-diones with phosphorus pentachloride turned out to be unusual [95, 96]. Dilthey [96] established that on boiling a solution of the pentaphenyl-substituted diketone **3** (benzomaron) in chlorobenzene 2,3,4,5,6-pentaphenylpyrylium chloride-hydrochloride **48** was formed, but di- and triphenyl-substituted diketones **3** at 18-20°C in absolute ether are converted into the corresponding pyrylium chlorophosphates **49** [95].



3 **48, 49**

3, 48 $R^1 = R^2 = R^3 = Ph$, X = Cl·HCl; **3, 49** $R^1 = R^3 = H$, R^2 = H, Ph, X = Cl·0.5 PCl_5

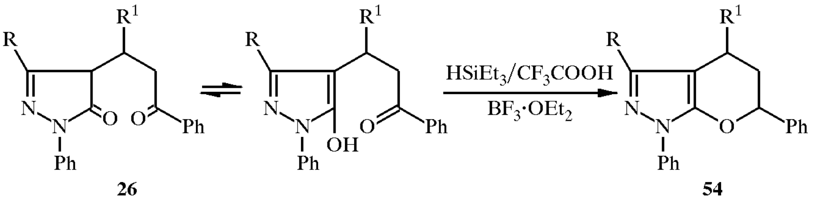
2. HETEROCYCLIZATION OF 1,5-DIKETONES UNDER IONIC HYDROGENATION CONDITIONS

1,5-Diketones of the alicyclic, semi-, and bicyclic series are cyclized on ionic hydrogenation with triethylsilane and trifluoroacetic acid, being converted into substituted tetrahydropyrans or their condensed analogs depending on the nature of the initial ketone [9, 97-101].

3, 6–10 **41, 42, 50–53**

3, 41 $R^1 = R^5 = Ph$, $R^2 = R^4$ = H, Me, $R^3 = H$, $R^2 = R^4 = Me$, $R^3 = H$; **6, 50** $R^1 = R^2 = (CH_2)_3$, $R^3 = R^4 = R^5 = H$; **7, 51** $R^1+R^2 = (CH_2)_4$, $R^3 = R^4 = H$, R^5 = H, Ph; **8, 52** $R^1+R^2 = R^4+R^5 = (CH_2)_3$, $R^3 = H$; **9, 53** $R^1+R^2 = (CH_2)_3$, $R^4+R^5 = (CH_2)_4$, $R^3 = H$; **10, 42** $R^1+R^2 = R^4+R^5 = (CH_2)_4$, $R^3 = H$

Oxopropylpyrazolones **26** undergo heterocyclization on hydrogenation with the reagents named above, in the presence of catalytic amounts of boron trifluoride etherate, with the formation of substituted 5,6-dihydropyrano[3,2-*d*]pyrazoles **54** [27, 98, 99].

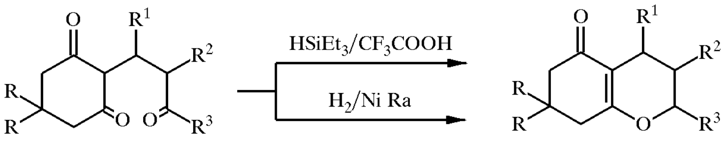


26 **54**

26, 54 R = Me, R^1 = Ph, *m*-$O_2NC_6H_4$, *p*-$MeOC_6H_4$;
R = Ph, R^1 = Ph, *m*-$O_2NC_6H_4$, *p*-$MeOC_6H_4$

The presence of catalytic amounts of boron trifluoride etherate, accelerating the ionic hydrogenation reaction, is necessary only in the case of 3-methyl substituted oxopropylpyrazolones **26**. When R = Ph the ionic hydrogenation of compounds **26** may also occur without a catalyst.

Ionic hydrogenation of triketones of the semi- **22** and bicyclic **55** series, containing a 1,5-dicarbonyl fragment, is carried out at 20°C with subsequent heating to 80°C. Under these conditions 5-oxohexahydrochromenes **56** and 5-oxodecahydroxanthenes **57** respectively are obtained in ~75% yield [101].



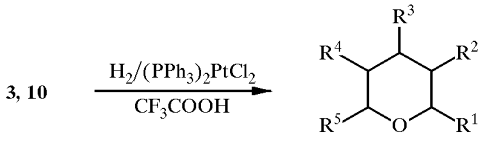
22, 55 **56, 57**

22, 56 R = H, Me, $R^1 = R^3$ = Ph, R^2 = H; R = Me, $R^1 = R^2$ = H, R^3 = Ph, *p*-$MeOC_6H_4$; **55, 57** R = H, Me, R^1 = H, $R^2 + R^3 = (CH_2)_4$

3. HETEROCYCLIZATION OF 1,5-DIKETONES UNDER CATALYTIC HYDROGENATION CONDITIONS

The semi- and bicyclic diketones **22** and **55** are converted exclusively and selectively into compounds **56** and **57** on Raney nickel catalyst at 50°C and a hydrogen pressure of 140 atm in alkaline medium [101].

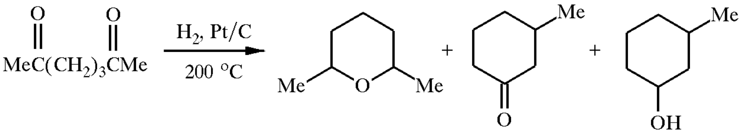
The heterocyclization of diketones **3** and **10** with the formation of a tetrahydropyran ring is observed under the action of CF_3COOH and molecular hydrogen at 30-70°C and ~200 atm pressure in the presence of catalytic amounts of complexes of platinum dichloride with triphenylphosphine [9,102].



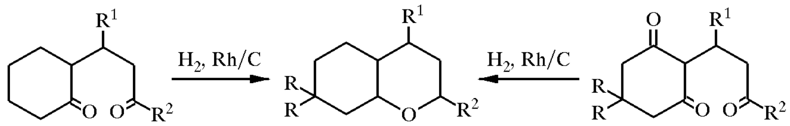
41, 42

3, 41 $R^1 = R^5$ = Ph, $R^2 = R^4$ = H, Me, R^3 = Me, H;
10, 42 $R^1 + R^2 = R^4 + R^5 = (CH_2)_4$, R^3 = H

On hydrogenating 2,6-dimethylheptane-2,6-dione over platinum on carbon at 200°C, 2,6-dimethyltetrahydropyran was formed [103].



However the process occurs nonselectively and in the reaction mixture there were also reduction products of compounds arising from the intramolecular carbo-cyclization of the initial 1,5-diketone, *viz.* 3-methylcyclohexanone and 3-methylcyclohexanol. The tetrahydropyran ring is formed on hydrogenation of the semicylic 1,5-diketones **7** and triketones **22** using Adams copper-chromium catalyst (200°C) and 10% rhodium on carbon (50-170°C, 8.08-10.10 MPa) [104,105].



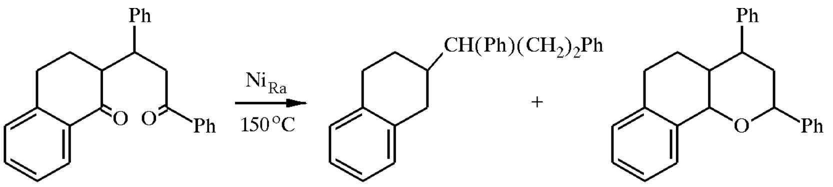
7 **51, 58** **22**

7, 22, 51 R = H, R^1 = Ph, *p*-$MeOC_6H_4$; **7, 51** R = H, R^1 = Ph, R^2 = *p*-$MeOC_6H_4$; R^1 = H, R^2 = Ph;
22, 51 R = H, Me, $R^1 = R^2$ = *p*-$MeOC_6H_4$; **58** R = H, $R^1 = C_6H_{11}$, *p*-$MeOC_6H_4$, $R^2 = C_6H_{11}$;
$R^1 = C_6H_{11}$, *p*-$MeOC_6H_{10}$, R^2 = *p*-$MeOC_6H_{10}$

Complete reduction of the carbonyl group in the alicycle took place in addition to the cyclization of triketones **22**. The presence of methoxyl groups in the aryl substituents hindered the reduction and heterocyclization of di- and triketones **7** and **22** respectively giving a lower yield of perhydrochromanes **58**.

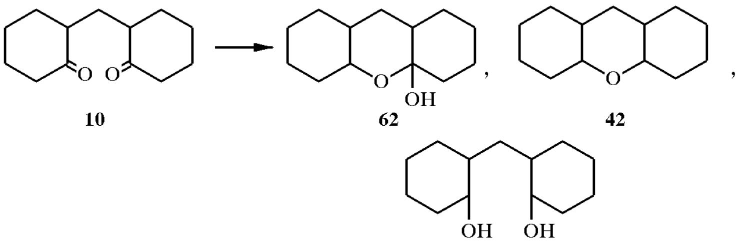
In difference to copper-chromium the rhodium catalyst enables the reduction of phenyl substituents to cyclohexyl. In the case of diaryl-substituted di- and triketones reduction of one Ph or two Ph, *p*-$MeOC_6H_4$ substituents occurs depending on the conditions. On hydrogenating diketones **7** containing *para*-methoxyphenyl substituents on a rhodium catalyst, and triketone **22** ($R = H$, $R^1 = Ph$, $R^2 =$ *p*-$MeOC_6H_4$) on copper-chromium, hydrogenolysis of the methoxyl group occurs [104-106].

In difference to the semicyclic 1,5-diketones **7** and **22** above, 2-(3-oxo-1,3-diphenylpropyl)-1-tetralone **59** undergoes carbonyl group reduction on catalytic hydrogenation on Ni_{Ra}, Rh/C, Ru/C at 100-150°C being converted into compound **60**. However heterocyclization, which leads to the corresponding tetrahydropyran **61** in ~20% yield, takes place only in acetic acid at 150°C on Ni_{Ra} [78].



59 **60** **61**

Data concerning the catalytic hydrogenation of alkylidene- and arylidenecyclanones, and also the products of their intramolecular carbocyclization, are widely reported in the literature. Carbocyclization occurs with the formation, depending on the conditions, of perhydroxanthenes **42**, 4a-hydroxyperhydroxanthenes **62** and/or 1,5-diols **63** [105,107-114].

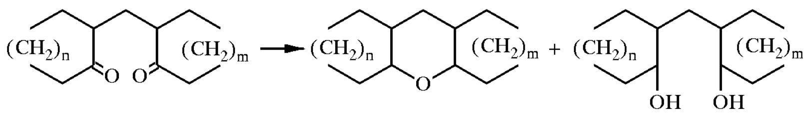


10 **62** **42** **63**

On hydrogenating the methylenedicyclohexanone **10** in the presence of Adams platinum catalyst, 5% Ru/C (alkali, at atmospheric pressure), and Ni_{Ra} the main product is the hemiacetal 1-hydroxyperhydroxanthene **62** predominantly of the *cis-anti-trans* configuration [107-109,111].

The use of catalysts obtained in acidic medium (5% Rh/C, 5% Ru/C, and 5% Pd/C) leads to an almost quantitative yield of perhydroxanthene **42** (80-92%) [110]. On forming the latter in the presence of rhodium catalyst a mixture of the *trans-anti-cis* and *cis-syn-cis* isomers is obtained [107,114].

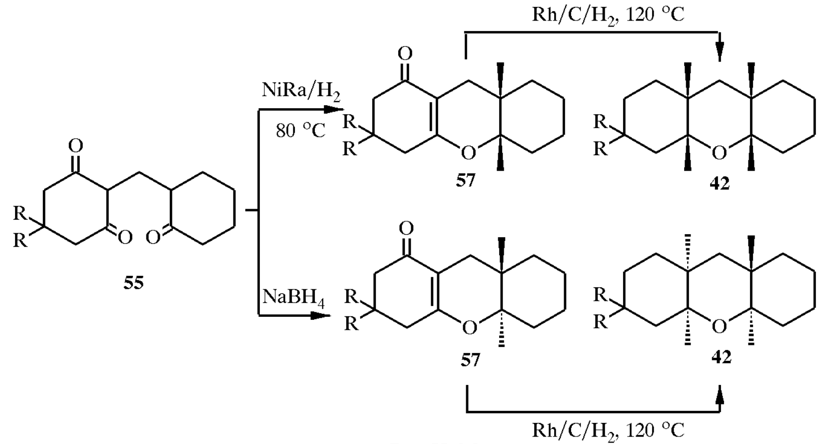
2-Oxocyclopentyl(or 2-oxocyclohexyl)methane **9** and especially methylenedicyclopentanone **8** are heterocyclized on catalytic hydrogenation with more difficulty and at a lower rate than methylenedicyclohexanone **10,** which is evidently linked with the rigidity of the structure.



8,9 **52, 53** **64, 65**

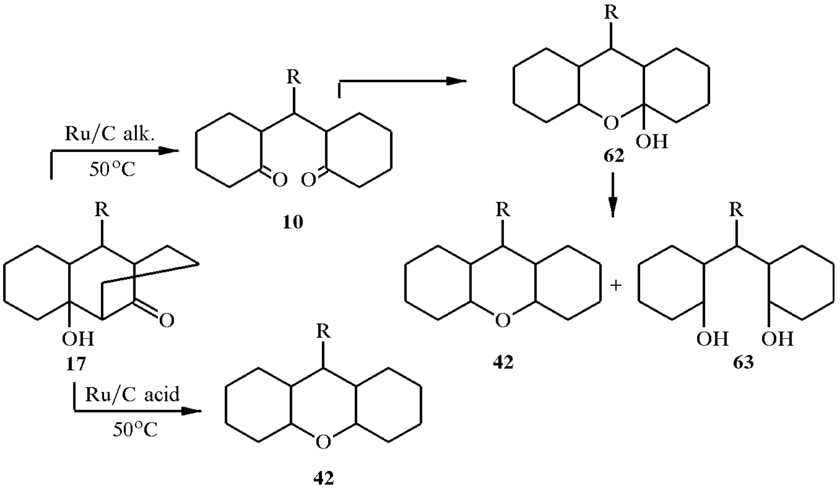
The condensed tetrahydropyrans **52** and **53** formed in this way have the configurations indicated above for compound **42**. A catalyst, such as Ru/C, prepared in alkaline medium enables the formation of mainly diols **64** and **65**.

Bicyclic oxo-1,5-diketones also undergo heterocyclization onto oxygen on catalytic hydrogenation. 2-[(2-Oxocyclohexyl)methyl]-1,3-cyclohexanedione **55** and its 5,5-dimethyl derivative are converted on Raney nickel in alkali at 80°C and hydrogen pressure 10.1 MPa predominantly into *cis*-1-oxodecahydroxanthene **57**. On rhodium catalyst at 120°C the latter forms *cis-syn-cis*-perhydroxanthene **42**. On chemical reduction with sodium borohydride *trans*-1-oxodecahydroxanthene **57** is obtained which is converted on rhodium catalyst at 120°C *into cis-anti-trans*-perhydroxanthene **42** [105].



55, 57, 42 R = H, Me

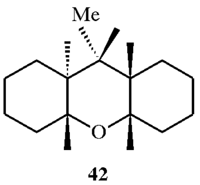
9R-Substituted perhydroxanthenes may be obtained from tricyclic β-ketols **17** (R = H, Me, Ph), distinguished by the ability to undergo retroaldol fission with the formation of the corresponding 1,5-diketones **10**.



R = H, Me, Ph

The decyclization of β-ketols **17** occurs under mild conditions. In the presence of 5% Ru/C (alk.) at 50°C in hexane the reduction leads to the hemiacetal **62**, which at 100°C is converted in the presence of the same catalyst into perhydroxanthene **42** and diol **63**. On hydrogenating over 5% Ru/C, obtained under acid conditions, at 50°C for 4 h and then at 100°C for 1 h, only perhydroxanthene **42** is formed.

The rate of reduction of β-ketols falls in the series R = H > Me > Ph. According to ^{13}C NMR data, 9-methylperhydroxanthene **42** is a mixture of 9β-methyl-*trans-anti-cis*- and 9β-methyl-*cis-syn-cis*-isomers [105,113,115].



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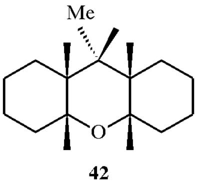

42

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