REACTIONS OF α- AND γ-ALKYL GROUPS IN PYRYLIUM

SALTS AND SOME TRANSFORMATIONS REACTION PRODUCTS

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Pyrylium salts having π-electronic sextet and de-
localized positive charge represent the particular
class of aromatic compounds showing high reactivity.
They are widely applied in organic syntheses and, on
the other hand, are the naturally occurring plant
compounds. This is why the chemistry of pyrylium
salts has received a great deal of attention. This
review will be generally confined to a discussion of
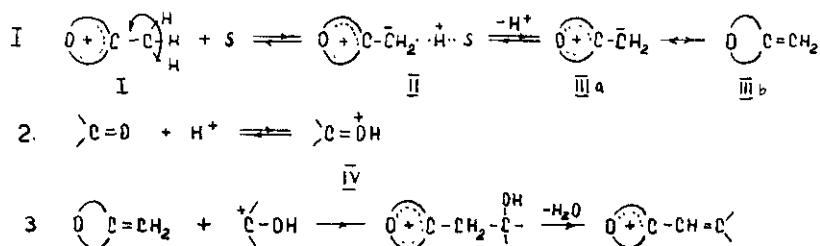certain reactions of pyrylium salts.

1. Reactivity of Methylpyrylium Salts and General Patterns of
   Their Chemical Behavior.

   Pyrylium salts having α- or γ-methyl substituents are known
to possess high reactivity to many electrophilic reagents, such
as aldehydes, pyrones, nitroso-compounds etc.[1-5]
The reactivity of α- and γ-methyl groups is due to their con-
jugation with the carbonium ion resulting by strong polarization
of the C-H bonds and hence in C-H acidity of these groups. So
the methylpyrylium salts can dissociate to methylene pyrans III
and proton in polar medium (Scheme I). Formation of methylene-
pyrans may occur by a solvent as well as by a basic reagent.

In most reactions the proton cleavage causes activation of
the pyrylium salts followed by the formation of methylenepyran
IIIb and the reagent involved the protonation of the latter, IV.

Reactions of pyrylium salts with carbonyl compounds serve
a useful example.

Scheme 1

Methylenepyrans formed in the dissociation of pyrylium salts
are the active species responsible for most reactions of methyl
groups of pyrylium salts. Methylenepyrans are essentially
heterocyclic analogues of vinyl alkyl ether and divinyl ether[6].

Similarly to the case of alkyl vinyl ethers, due to the +M-
effect of the oxygen atom and the enhanced electron density at
the methylene carbon atom influence high nucleophilicity of me-
thylenepyrans[5]. The simplest monocyclic methylenepyrans are
unstable, readily undergoing oxidation in the air and very
difficult to isolate in a free state[7,8].

Methylenepyrans having electron withdrawing substituents in
the methylene group (V)[4,9,10] as well as these with more extended
conjugation chains [condensed methylenepyrans (VI)[11-13]] or
sterically hindered species (VII)[7] show higher stabilities.
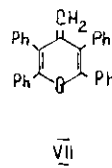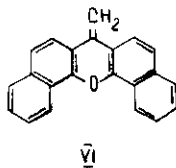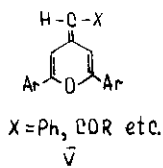
Metylenepyrans containing two electron withdrawing groups are even more stable[14-16], e.g..
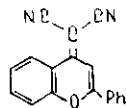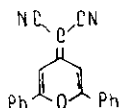
Mono- and polymethine cyanines containing the pyrylium cation as an electron accepting group also belong to compounds of type III[2,17,18].
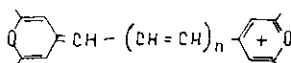
Although basicity of methylenepyrans might be used as a measure of their reactivity, quantitative data of this kind are inavailable. Only recently, on the basis of indirect measurement, the basicity of methylenepyran formed from 2,4,6-trimethylpyryrium salt was tentatively evaluated to be of 12 to 14 pK_a[8].

High basicity of methylenepyrans including conjugated cations (cyanines)[19] can be inferred from the fact that all of them easily undergo protonation to pyrylium salts by mineral acids[9,20]. Quite a number of examples illustrate their reactivity towards positively charged or electron deficient species. Thus, there are data[11] on reactions involving the attack on the methylene unit by the nitronium and nitrosyl cations, and aliphatic and aromatic carbonium ions.

Calculations of electronic density distributions in various pyrylium cations and in the corresponding methylenepyrans[21-24] show the α-methyl group of pyrylium salts to bear a higher positive charge than the γ-methyl group, and α-methylenepyrans to be thermodynamically favoured over the γ-substituted species. The calculational results for methylpyrylium cations correlate well with the methyl proton chemical shifts observed in proton NMR spectra[25,26]. The lower the electron density is at the methyl carbon atom, the higher field is the chemical shift. The following data[21] give the

chemical shift (δ scale) as electron density dependence for the 2,3,4,6-tetramethylpyrylium cation.
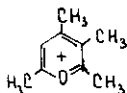
| Substituent position	α-CH$_3$	γ-CH$_3$	β-CH$_3$
Electron density	1.9343	1.9404	1.9606
δ	2.88	2.69	2.43

Therefore, it is reasonable to expect the preponderant formation of the α-isomer in a condensation reaction. However, the experimental data[19] show 2,4,6-trimethyl and 2,4-dimethyl-6-phenylpyrylium salts to condense with carbonyl compounds with the exclusive formation of the γ-substituted products[19].
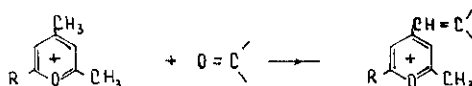

R is CH$_3$ or C$_6$H$_5$.

This result is consistent with the isotopic exchange experiments[27] including the deuteration experiments[28]. The deuteration proceeds 10 times faster with the γ-methyl group than with the α-methyl group.

Thus the α-methyl groups having higher calculated acidity are proved to be less reactive in the condensation reactions and isotopic exchange processes. The result of deprotonation of 2,4-dimethyl-3-azapyrylium salts appears even more difficult to rationalize. It has been shown[29,30] that triethylamine reacts with these compounds to yield exclusively 4-methylene-3-azapyrans, though the 2-methyl group should possess the highest acidity according to calculations.
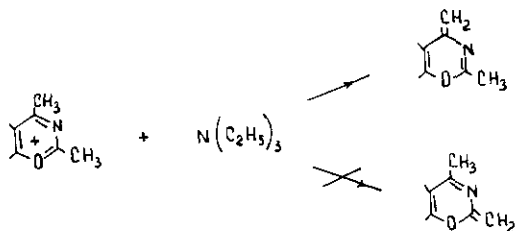
On the contrary, pyrimidinium salts possessing similar electronic structure to that of 3-azapyrylium salts undergo deprotonation at its 2-methyl group[30].
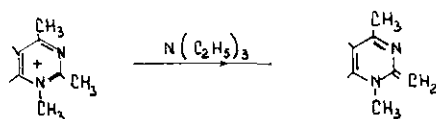

This unusual behavior appears to be characteristic of six-membered oxonium heterocycles and may be due either to limitanions of calculational procedures applied or to the great difference in electronic structure as compared with those of the base state.

Methyl groups of pyrylium salts have been shown to be more reactive than those of pyridinium salts[3,31]. There are data, though purely qualitatively, on the influence of structure of pyrylium salts on the methyl groups reactivity[32]. Thus, the α-mehtylene group is believed to be more reactive, as compared with the α-methyl one[33], and electron withdrawing substituents in the nucleus supposed to facilitate reactions of methyl group[3].

In the pyrylium salts having two or three activated methyl groups only one of them readily reacts in middle conditions while condensations involving two or three methyl groups require much more rigid conditions[19,31,34].

2. Reactions of Methylpyrylium Salts with Carbonyl Compounds.
a) Condensations with Aldehydes: Methylpyrylium salts readily react with aldehydes to give the respective β-arylvinyl derivatives[35-40].

$$\text{O}^{+}\text{C-CH}_3 \quad + \quad \text{R-CHO} \quad \longrightarrow \quad \text{O}^{+}\text{C-CH=CH-R}$$
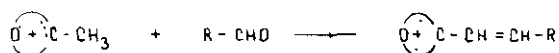
It is hardly to discuss the optimum reaction conditions as these were widely varied and nearly quantitative yields were obtained in all cases. Thus, benzopyrylium salts undergo condensation at ambient temperature $(20^{\circ}C)$ [41] and at elevated temperatures [42], in neutral [43] and strongly acidic [41,42,43,45] media, or in the presence of bases [46]. Alcohol, formic acid, and acetic anhydride are used as solvents.

Dilthey and Fischer [1,35] were the first to report on the condensation of monocyclic pyrylium salts with aldehydes. They obtained the styrylpyrylium salts from aromatic aldehydes and 2,4-diphenyl-6-methyl- and 2,6-diphenyl-4-methylpyrylium salts in refluxing acetic acid or acetic anhydride.
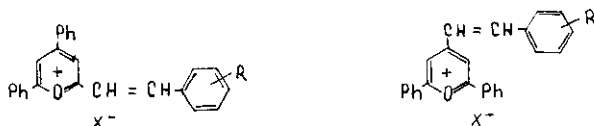
Later [39], the reaction was extended to a wider range of aromatic aldehydes to show that electron donating substituents in the aldehyde nuclei facilitate the condensation [32,39]. Keleman and Wizinger [39] found aromatic aldehydes to react with 2,6-diethyl-4-methylpyrylium perchlorate exclusively at the 4-methyl group, while the α-methylene groups remained intact. According to these authors, the 4-methyl group of the 4-methyl-2,6-diisopropylpyrylium cation was more reactive than that of the 4-methyl-2,6-diethyl derivative.

Dorofeenko and co-workers [47-49] studied reactions of pyrylium salts with a variety of aliphatic, aromatic and heterocyclic aldehydes, and were the first to process the condensation with the aliphatic compounds.

In the case of pyrylium salts bearing the α-methyl as well as α-methylene groups, the latter was proved to be more reactive in the condensation with aldehydes [33].
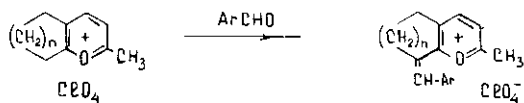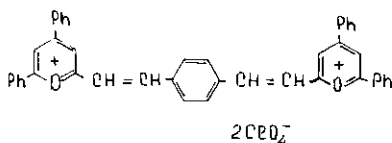
Aldehydes of the azulene series readily condense with methyl-pyrylium salts in refluxing acetic acid[32].
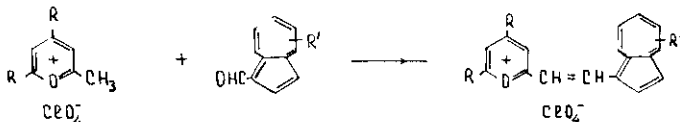
The substituent R in the pyrylium nucleus are shown to increase the reactivity of the α-methyl group in the order: $C_6H_5 < C_4H_3S < 3,4-(CH_3O)_2C_6H_3$.
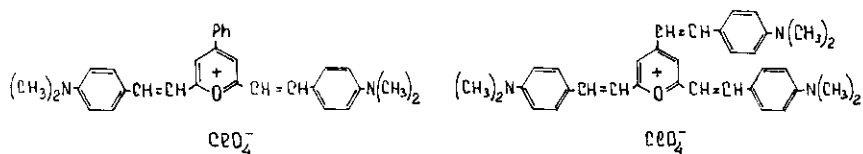
Terephthalic aldehyde reacted with both aldehyde functions to give the bis-product[50].

Earlier, 2,4,6-trimethylpyrylium perchlorate was thought to give a mixture of α- and γ-isomers in condensations with aromatic aldehydes. More recent data showed 2,4,6-trimethyl- and 2,4-dimethyl-6-phenylpyrylium salts to react with p-dimethylamino-benzaldehyde exclusively through the γ-methyl group, thus this evidences the latter to be more reactive than the α-methyl group[19].
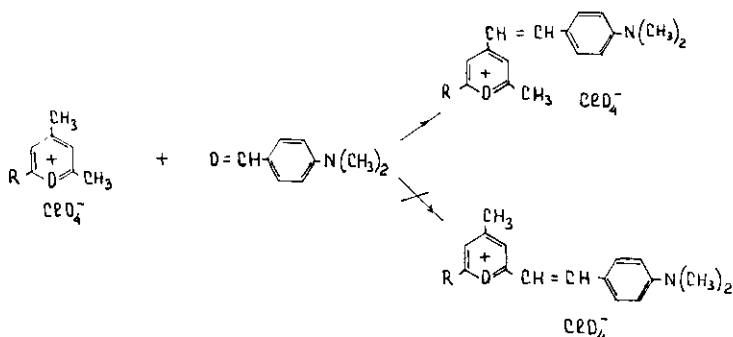
The same reaction afforded di- and tri-styrylpyrylium salts under more drastic conditions[34].

$(CH_3)_2N$—CH=CH—$\overset{Ph}{\underset{O^+}{\bigcirc}}$—CH=CH—$N(CH_3)_2$ ClO_4^-

$(CH_3)_2N$—CH=CH—$\overset{CH=CH—N(CH_3)_2}{\underset{O^+}{\bigcirc}}$—CH=CH—$N(CH_3)_2$ ClO_4^-

The benzopyrylium salts containing one α or γ methyl substituent reacted with aldehydes under milder conditions compared to mono-cyclic cations. Borsche and co-workers[41,53] reported the first illustration to condense aromatic aldehydes with methylpyrylium salts of the benzopyrylium series. Later, the reaction was extended to other benzopyrylium cations[18,42-44,46,53-55].

Heilbron, Walker and Buck[45] studied the condensation of 2,4-dimethylbenzopyrylium salts with aromatic aldehydes to show that the isolated monostyryl derivatives were not mixtures of α- and γ-isomers; however they could not assign any particular structure to the products.

The above cited results[19] of Strzelecka and co-workers on reactions of monocyclic pyrylium salts favoured the γ-isomer for the products obtained by Heilbron; however, this supposition should be verified.

Condensation of methylpyrylium salts with heteroaromatic aldehydes such as N-methylindole-3-aldehyde and 3-formylflavene was also reported[59].

Reactions of benzopyrylium salts with unsaturated aldehydes were described[54,60,61].

R-(CH=CH)$_n$-CHO   R = Ar, Het

FeCl$_4^-$ → FeCl$_4^-$ CH-(CH=CH)$_n$-R
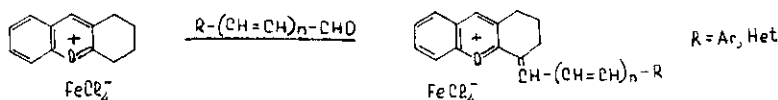
9-Methylxanthylium salts also condensed readily with benz-
aldehydes to give styrylxanthylium salts[11-13, 62].

CH=CH-Ar

X$^-$
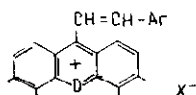
Kamel and Shoeb[11,12,62] and Lenke and co-workers[13] obtained
the 9-styryldibenzoxanthylium derivatives by refluxing acetic
anhydride solutions of 9-methyldibenzoxanthylium salts and p-
substituted benzaldehydes.

CH$_3$ R-⟨ ⟩-CHO →   CH=CH-⟨ ⟩-R

ClO$_4^-$ ClO$_4^-$
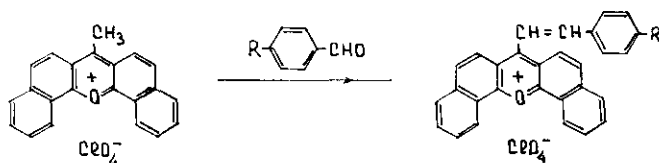
The condensation of methyldibenzoxanthylium salts with 9-
methylenedibenzoxanthene-ω-aldehyde led to trimethine dyes[11].

CH$_3$ +   CHO → CH=CH-CH

ClO$_4^-$ ClO$_4^-$
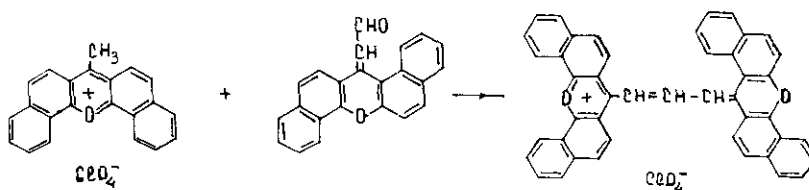
The characteristic feature of alkyl- or arylpyrylium salts was
applied for transformation to other aromatic compounds. Thus,
monocyclic styryl derivatives easily exchange their heterocyclic
oxygen atom for the sulfur atom when treated with sodium sulfide[63,64]

CH=CH-Ar   CH=CH-Ar

Ph—O—Ph   Na$_2$S→   Ph—S—Ph

ClO$_4^-$ ClO$_4^-$
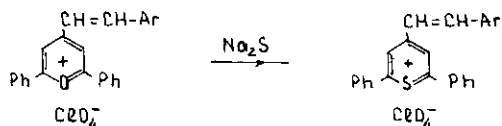
The interaction of styrylpyrylium salts with ammonia leads to
styryl substituted pyridines[46,48].

Ph—O—CH=CH-R   NH$_3$→   Ph—N—CH=CH-R

ClO$_4^-$
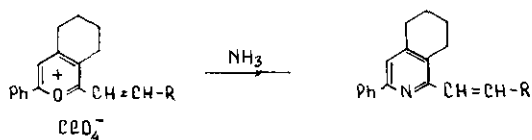
Styrylpyrylium salts containing α-methyl groups give dialkyl-aminostilbenes under the action of secondary amines (diethyl- and dimethylamine, morpholine and piperidine)[51,52].
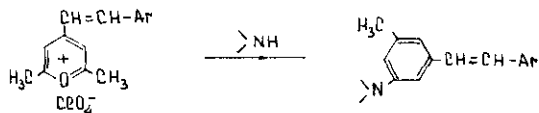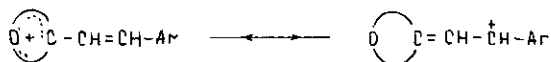

The action of bases on styrylpyrylium salts containing hydroxyl functions in the aromatic ring results in the formation of deeply coloured compounds of quinonoid structure[42,44,56].
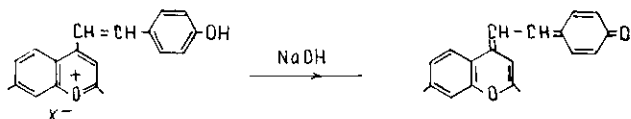

The condensation products from o-hydroxybenzaldehyde give spiropyrans under the action of bases[57,58].
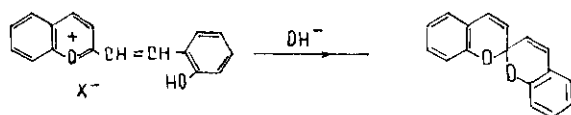


The presense of the β-arylvinyl group in styrylpyrylium salts explains their peculiar chemical behavior as depending on the occurrence of positive charge on the vinyl carbon atom[65].

There exist data on reactions of 2- and 4-styrylpyrylium salts with aldehydes and pyrones in acetic anhydride solutions[65-67]. The action of 2,6-diphenyl-4-styrylpyrylium with p-dimethylamino-benzaldehyde privides an instructive example[65].
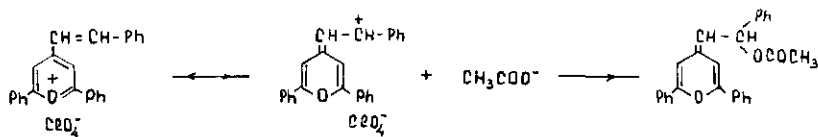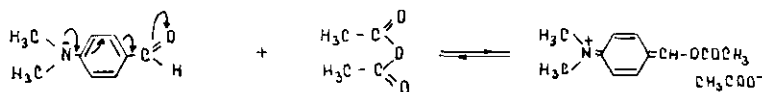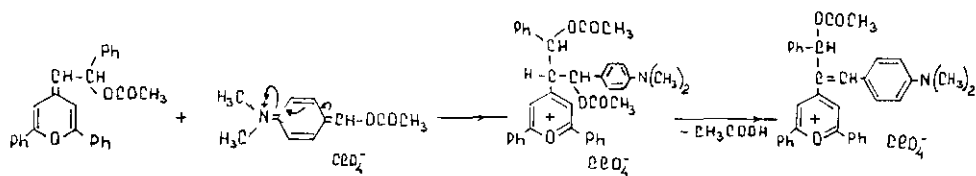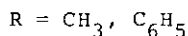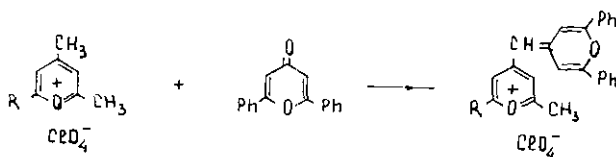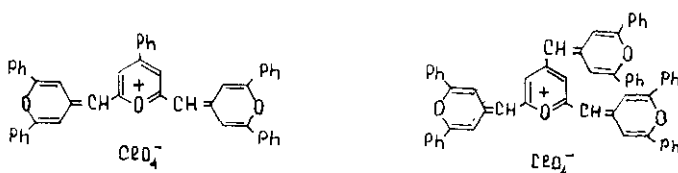
Scheme 2

Styrylpyrylium salts are the deeply coloured compounds, and their colouration deepens in going from aliphatic to aromatic and hetero-cyclic radicals[47].

The occurrence of electron donating substituents in the styryl residue causes bathochromic shifts in their UV spectra which in-crease in the series m < o < p, whereas electron withdrawing groups have the opposite effect[49,55,60,68-77].

b) Condensations with Pyrones: Pyrones, thiapyrones, benzopyrones and xanthones condense with pyrylium salts containing activated methyl and methylene groups to produce monomethine cyanines. Usually, the process occurs in refluxing acetic anhydride. The pyrylium salts containing two or three activated methyl groups usually react through the γ methyl group with the 1 : 1 reactants ratio[19].

R = CH$_3$, C$_6$H$_5$

The participation of two or three methyl functions can be achieved by changing the reactant ratio[34].

The following reaction mechanism has been suggested[78].
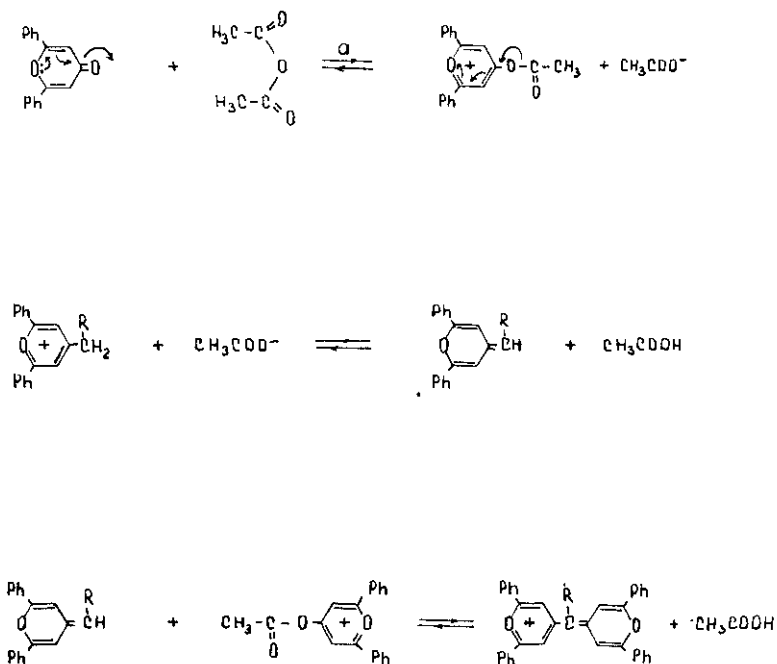
Scheme 3

The authors[78] believe that successful development of the process requires acetate ions to be removed, to shift the equilibrium a to the right by proton cleavage from the pyrylium salt with the ion. To verify this supposition, the authors have studied the condensation of 2,6-diphenyl-4-phenylmethylenepyran with 2,6-dimethylpyrone in acetic anhydride.
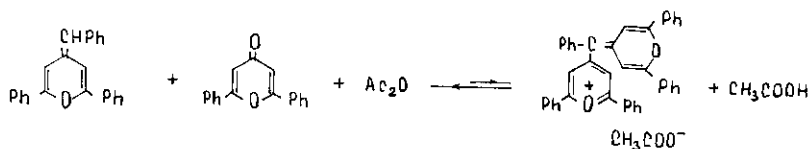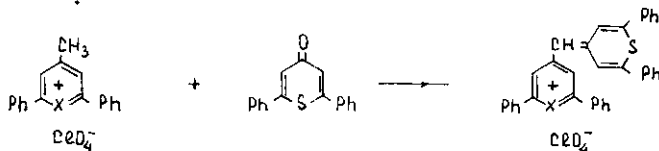

The UV spectra show that no monomethine cyanine occurs under such conditions. On the other hand, the introduction of sodium or lithium ions removing the anions affords the expected cyanine in a high yield[79-81].

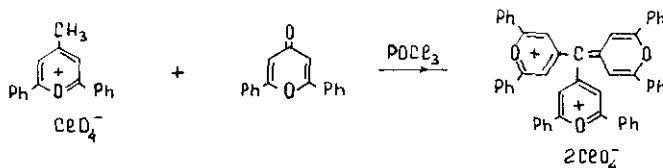Phenacylpyrylium salts easily condense with pyrones[9].
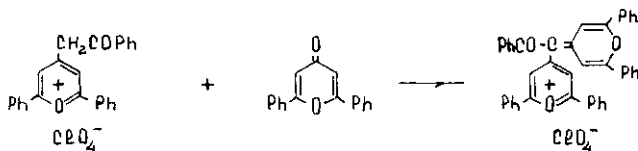
Thiapyrons react similarly to methylpyrylium and thiapyrylium salts[62,82,83].

X = O or S

Van Allan and Reynolds[84,85] obtained trinuclear dyes by running the condensation in phosphorus oxychloride.

Wizinger and co-workers extended the reaction to flavones[86], xanthones[87] and coumarins[88,89] to obtain monomethine dyes.
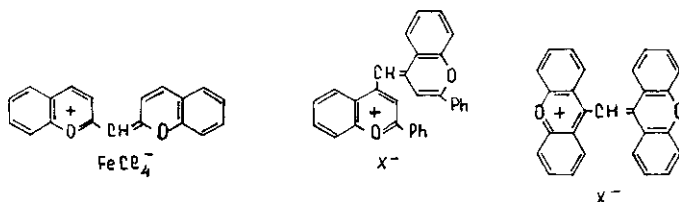
| VIII | IX | X |

Condensations with coumarins and xanthones were run in the presence of phosphorus pentachloride. The process appears to involve the intermediate formation of chloropyrylium salts. Synthesis of pyryl cyanines from arylidene- and heteroarylidenepyrans with chloropyrylium salts supports this conclusion[90,91].

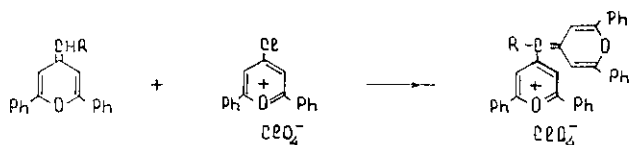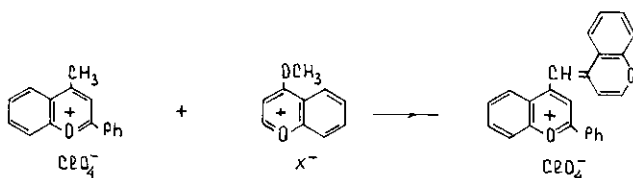The interactions of various xanthones with dibenzoxanthylium salts are also described[12,62]. The 4-alkoxybenzopyrylium salts which are derivatives of benzopyrones were also be shown[82] to condense with the methylpyrylium salts.

This reaction provides an indirect evidence for the above mechanism involving the formation of acyloxypyrylium salts from pyrones. 2,6-Dimethyl-4-alkoxypyrylium perchlorate undergoes condensation to monomethine cyanines in the presense of organic and inorganic bases[92,93].
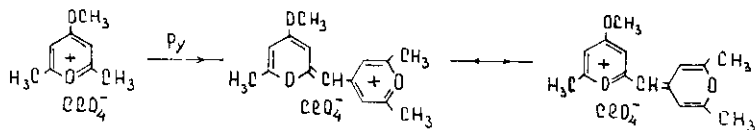
Monomethine cyanines formed in the condensation of pyrones with methylpyrylium salts exhibit behavior characteristic of both methylenepyrans and pyrylium salts.

Thus strong acids protonate them to pyrylium dications[19]. The introduction of water or alcohol causes regeneration of pyryl cyanines.
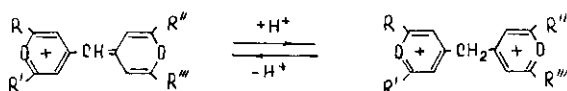
The heterocyclic oxygen atom can be replaced with nitrogen by the action of ammonia or primary amines[93,94].

The treatment with sodium sulfide in acetone solution results in the substitution of one of the oxygen atoms by sulfur[94,95]. However, this reaction will not go with the pyrylium salts having the α-methyl substituent[63].

UV studies of monomethine cyanines show that the lesser is the difference in the basicity of the two nuclei involved, the deeper is colouration of the compound[56,63,82,96-99].
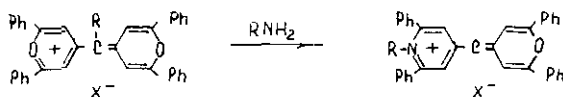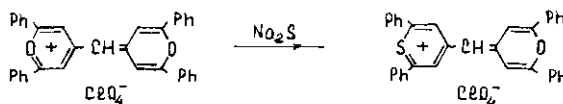
c) Condensation with Dimethylformamide. Reynolds and Van Allan have shown[100,101] that heating 2- and 4-methyl pyrylium and benzopyrylium salts with N,N-dialkylformamide in acetic anhydride affords N,N-dialkylaminovinyl derivatives.
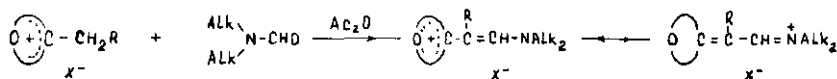
Condensations have been run under standard conditions for 15 min in refluxing acetic anhydride and the yields can serve to compare reactivities of alkyl groups in this reaction. The reported data demonstrate that, of α-alkyl derivatives, the methylene group of hydrogeneted ring XI exhibits the highest reactivity, then follows the methylene fragment of the ethyl group XII, and the α-methyl group of compound XIII is the least reactive one. The initial salts are as follows.
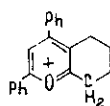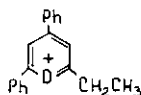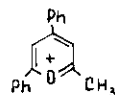
XI   XII   XIII

The yields of aminovinylpyrylium salt from the compounds XI, XII and XIII are 91 %, 73 % and 38 %, respectively.

Reactivity of α- and γ-methyl groups depends on the structure of the salt. When the initial salts are as follows, the yields of amino-vinylpyrylium salts are 90 %, 76 % and 38 %, respectively.
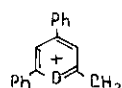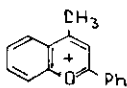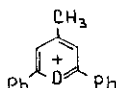
More recently the reaction mechanism shown in Scheme 4 has been suggested[102].
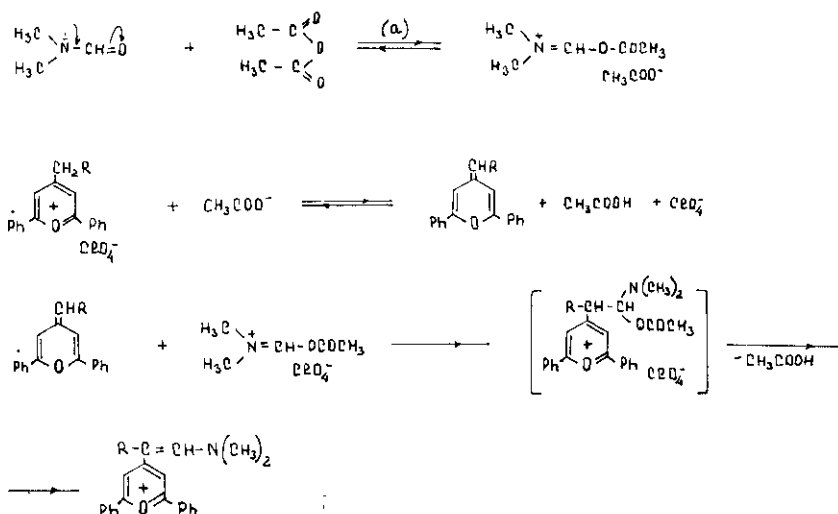
Scheme 4

According to the Scheme, the development of the reaction depends on the equilibrium (a) which is strongly shifted on the

left in the absence of agents removing the acetate anion (in the case shown in the Scheme, abstraction of the hydrogen of methyl group from the pyrylium salt provides such an agent).

This is the reason why methylenepyran reacts with N,N-dimethylformamide in acetic anhydride to give only a trace amount of aminovinyl salt (XIV), whereas the reaction goes in high yields with acetate ions removed by alkali metal cations.
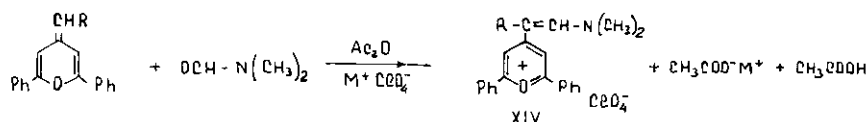
Attempts to use N,N-dimethylacetamide in this reaction were unsuccessful, dimethylthioacetamide however reacted to give the corresponding salts[100].
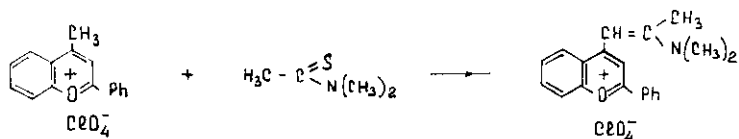
9-Methylxanthylium salts condense with N-methyl-N-phenyl-formamide to give N-methyl-N-phenylaminovinylxanthylium derivatives[103].
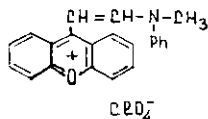
Heating 4-methylflavylium diphenylformamide results in the removal of the aniline molecule to afford 4-N-phenylaminovinyl-flavylium perchlorate[17].
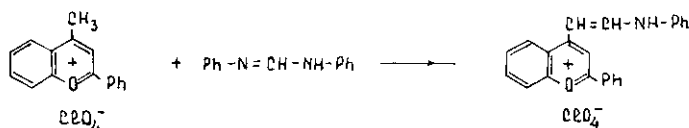
N,N-Dialkylformamide reacts with monocyclic 2- and 4-methylpyry-lium and 4-methylbenzopyrylium salts in the presense of phosphorus oxychloride to give bis-aminovinyl derivatives[100,101].
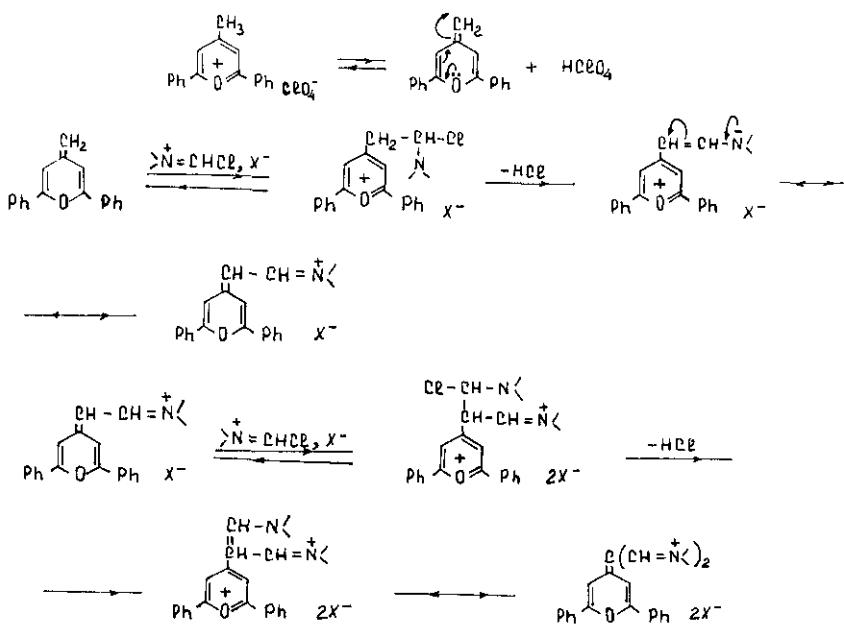
Scheme 5

The unusual formation of monoaminovinyl derivatives under the same conditions is observed in the case of 2-ethylpyrylium salts.

N,N-Disubstituted amides of aliphatic and aromatic carboxylic acids also condense with alkylpyrylium salts in the presence of phosphorus oxychloride to give monoaminovinyl derivatives.

where R is H, CH_3
and R' is CH_3, C_6H_5
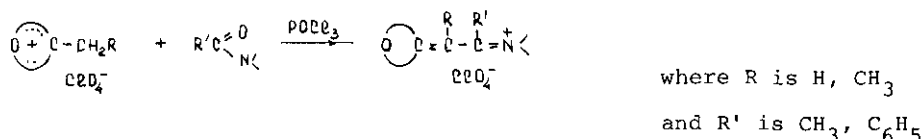
The difference in the behavior of dimethylformamide and disubstituted amides of other carboxylic acids is attributed to steric factors[100,104].

Vinylogs of dimethylformamide react to produce highly conjugated systems[60,100].
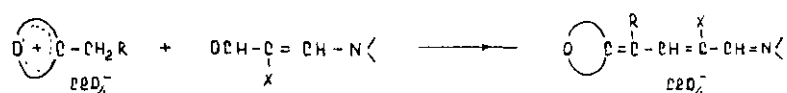
where X is Cl or Br.

In the case of N-phenylaminopolyvinylaldehydes, the condensation leads to cyanine dyes[17].
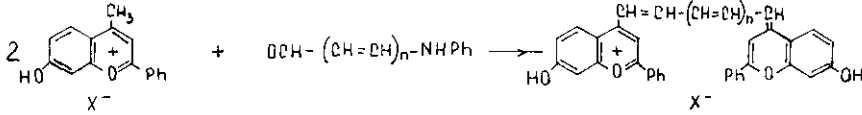
N,N-Dialkyl- and N-phenyl-substitued ω-amino acroleins react in a different way, probably due to far lower basicity of the nitrogen atom of the latter which results in higher positive charges on the terminal carbon atoms of the polyene chains of aminovinyl salts.

Aminovinylpyrylium salts give α,β-unsaturated aldehydes when treated with aqueous alkali. The aldehydes readily undergo protonation to the corresponding β-hydroxyvinyl derivatives[100,102,105].
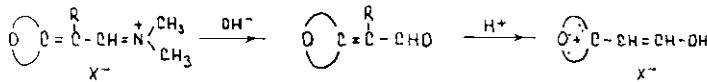
Hydrolysis of bis-aminovinyl salts under the same conditions leads to dialdehydes (XV) although in aqueous pyridine, saponification of only one imino function occurs to give XVI[100].

XV   XVI

Aminovinyl compounds are not hydrolized in acetic acid at room temperature. Heating them in aqueous acetic acid in the presence of perchloric acid does not afford the expected aldehydes since the latter decomposed to the alkylpyrylium salts under these conditions[102].
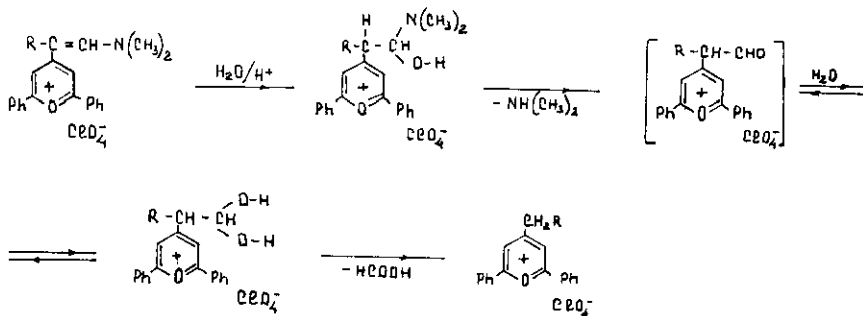
Aminovinylpyrylium salts react with aliphatic primary amines to give methylenepyridines[101]. In this reaction, the N,N-dimethyl group is replaced with the N-alkyl group of the attacking amine, while another molecule of the latter adds at the α-position of the pyrylium ring. Then the ring opening and transcyclization occur.
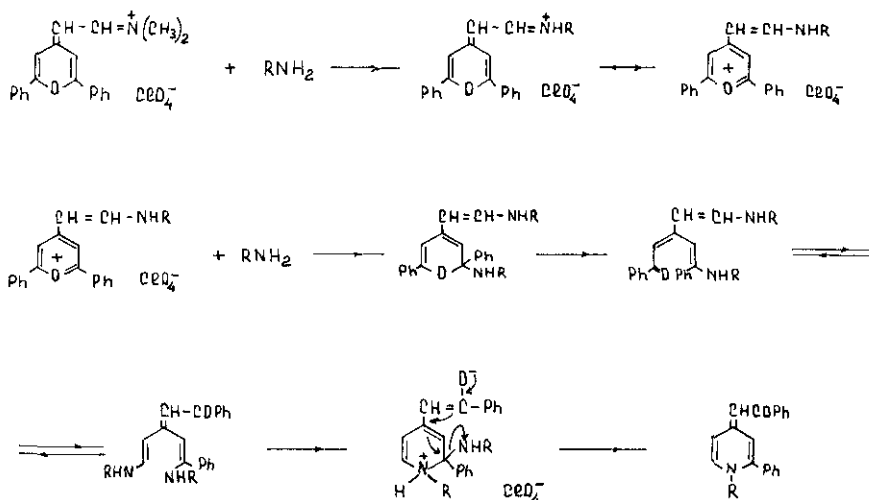
Reactions of 2- and 4-β-dimethylaminovinylpyrylium salts with secondary amines give rise to various products. Thus, 2-aminovinyl derivatives react with dimethylamine to give 4-dimethylamino-2-phenylbenzophenone[100].
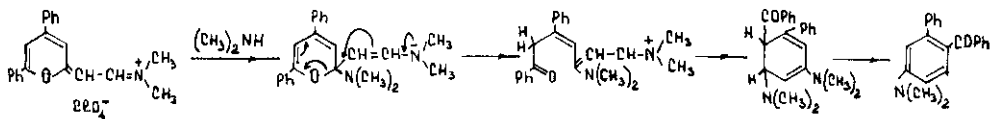
A similar reaction occurs under the action of sodium methoxide.

With 4-β-aminovinylpyrylium salts, the action of secondary amines leads to the replacement of the N,N-dimethyl function with the N,N-dialkyl one[101].
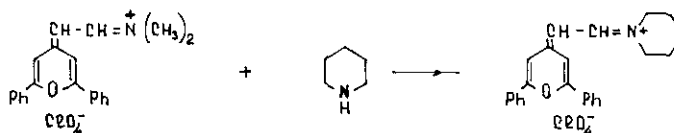
Bis-aminovinyl derivatives react with primary amines to give
diquaternized coperines[101].
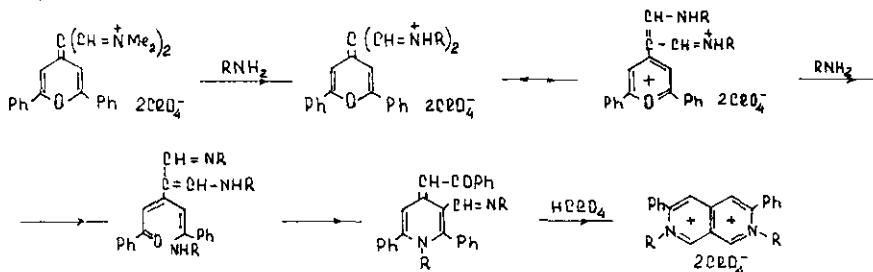
With ammonia, uncharged heterocycles are formed.
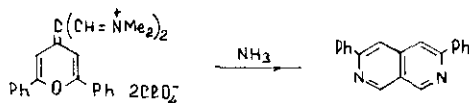
The reaction of piperidine with bis-aminovinyl salts leads to the
addition of three moles of piperidine. The product converts to the
bis-compound under the action of perchloric acid.
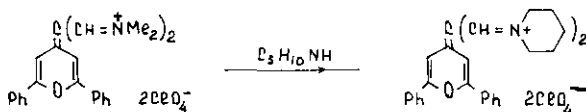
3. Reactions with Hetero Analogues of Carbonyl Compounds.

a) Reactions with Nitroso Compounds. Nitroso compounds behave
like aromatic aldehydes in reactions with methylpyrylium salts.

Simalty, Strzelecka and Khedija[106] carried out the condensation
of p-nitroso-N,N-dimethylaniline with mehtylene substituted
monocyclic pyrylium salts to show that the reaction led to the
Schiff bases.
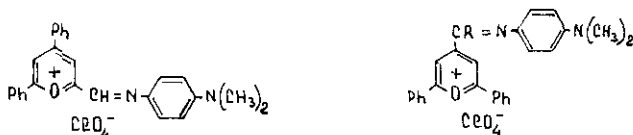
where R is H, C_6H_5 or COC_6H_5.

The authors[106] suggested the following reaction mechanism.

Scheme 7
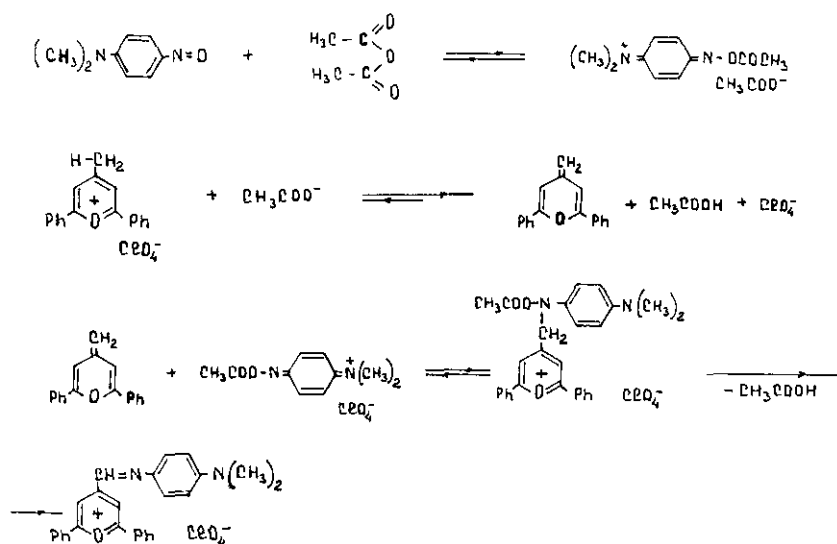
Similarly to the case of earlier studied reactions[78,102]
[See Section 2 (a)] the occurrence of equilibrium (a) was proved.
The addition of alkali metal salts[107] favoured the process, as
evidence by the UV spectral experiments. Thus, p-nitrosodimethyl-
aniline in acetonitrile solution absorbs at λ_{max} of 420 nm.
The addition of acetic anhydride causes no spectral changes, whereas
in the presence of lithium perchlorate, the band at λ_{max} 420 nm
disappeared and a new band at λ_{max} 322 nm characteristic of immonium
cation emerged. The role of lithium cation consisted in binding
acetate anions formed in the reaction. The UV spectral studies also
showed the reaction to require the presence of acetic anhydride.
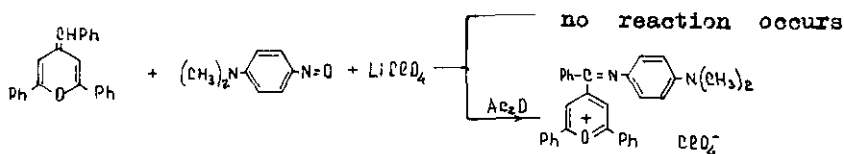
The reaction did not go in acetic acid or alcohol media[108].
The condensation of p-nitrosodimethylaniline with methylpyrylium
salts occurs when acetic anhydride-methylene chloride solution of the
reactants was allowed to stay for two hours at room temperauture.
The yields varied over the range 30 to 70 %[106].

The hydrolysis of ketimines with acids resulted in a formation ketones whereas aldimines remained unchanged under the same conditions.
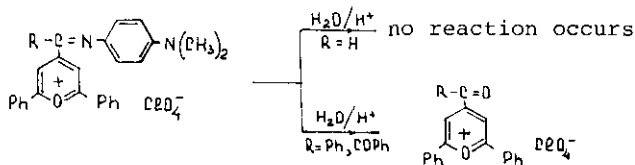
b) Reactions with Dimethyl Sulfoxide. Alkylpyrylium salts condense with dimethyl sulfoxide in refluxing acetic anhydride/methylene chloride mixture giving rise to sulfonium salts[109].
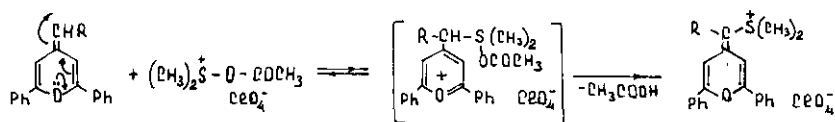
Scheme 8

Sulfo compounds were obtained in 70 to 80 % yields.

Heating a mixture of 4-methyl-2,6-diphenylpyrylium perchlorate with excess dimethyl sulfoxide for a longer period of time afforded the bis-products[109,110].
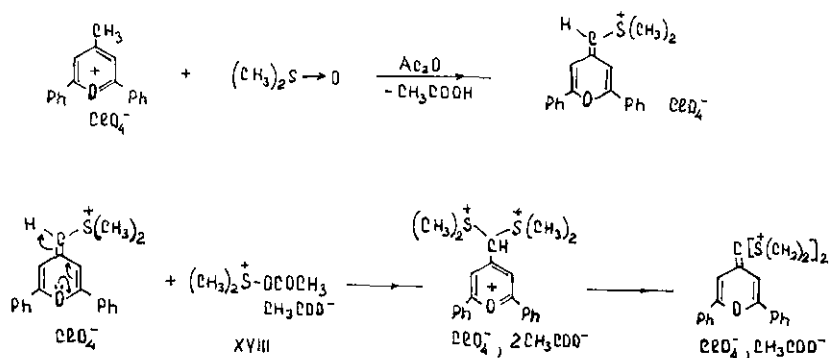
Scheme 9

The reaction of 2-methyl-4,6-diphenylpyrylium perchlorate could not be stopped at the stage of monocation formation. The yields of di-cationic salts increased two fold in the presence of alkali metal cations providing higher concentrations of acetoxysulfonium salts XVIII essential to reaction (a).

Sulfonium salts behave as bases and undergo protonation with *strong mineral acids to bis-cations.*
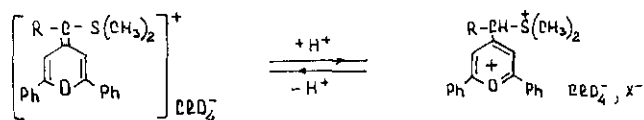
4. Interaction with Ortho Esters

Reactions of methylpyrylium salts with ortho esters provide the most widely used synthetic route to trimethine cyanines. Usually the reaction is run in refluxing acetic acid, acetic anhydride or pyridine. At present, the reaction mechanism shown in the following scheme is generally accepted.
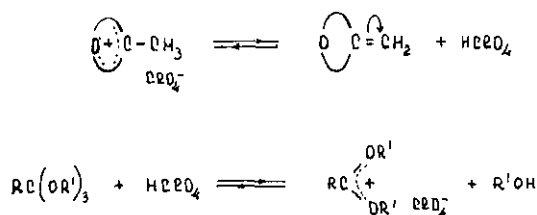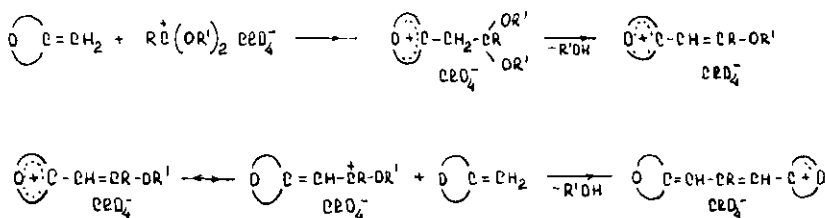
Scheme 10

Compounds XIX and XX described in papers[17,59,111] were the first example of trimethine dyes obtained from monocyclic pyrylium salts.
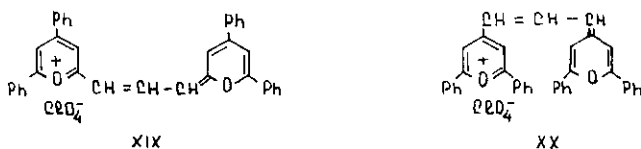
These compounds were synthesized by refluxing an acetic anhydride and pyridine solution of the reactions.

Benzylpyrylium salts reacted with orthoformate in a similar way[4,9].
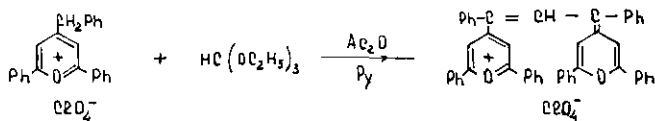
With phenacylpyrylium salts, the reaction led to cyanines XXI which converted to tri-cation tris-pyrylium structures under the action of perchloric acid[9,67,112].
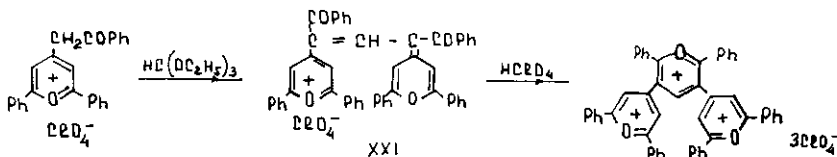
The treatment of XXI with ammonium acetate resulted in the replacement of two heterocyclic oxygen atoms by nitrogen, whereas ammonium carbonate caused the replacement of only one oxygen atom[67,94].
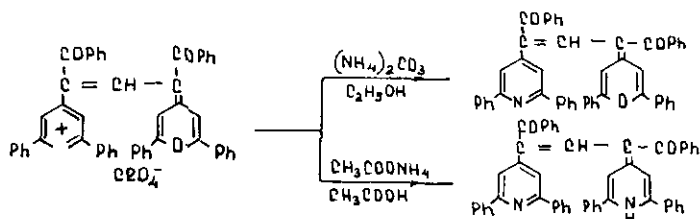
Attempts to the preparation of sulfur-substituted species by
sodium sulfide treatment of trimethines were unsuccessful because
the products could not be isolated in the pure form[95].

Benzopyrylium salts gave cyanine dyes under milder conditions.
A number of papers reported the preparation of pyryl cyanines from
2- and 4-methylbenzopyrylium[86,88,18,46] and 9-methylxanthylium[103]
salts. The use of esters other than ethyl orthoformate was
described[18,94]. When treated with aqueous alkali, benzopyrylium
cyanine dyes containing hydroxyl functions converted to the anhydro
bases[18].
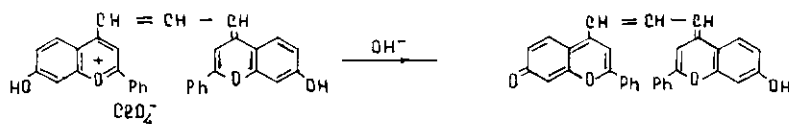
Papers[97,113] discuss the effect of cyanine structure on the
position of the band maxima in the UV spectra. Cyanine dyes are
deeply coloured and absorb in the long wave length region[2,17,89,114,115].
An increase in the basicity of heterocycles composing the cyanine
molecule as well as higher molecular symmetry was reported[17,24]
to favour a greater wave-length shift of the absorption bands.
Wizinger and co-workers[86,116,117] have studied bathochromic
effects in the UV spectra of cyanines as depending on the number
of the vinyl units in the polyene chain.
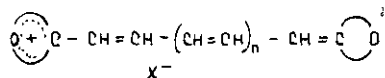
The maximum shift per vinyl unit occurs in going from $n = 0$ to
$n = 1$. However, convergence variations show that the dependence
is not a liner one.

Heating pyrylium salts containing the α-methylene group with
ethyl orthoformate affords 2-(β-ethoxyvinyl) derivatives[88,118,119].
Ethoxyvinylpyrylium salts also result from the condensation of α-
and γ-methylpyrylium, benzopyrylium, and xanthylium salts with

orthoformate in warm acetic acid or nitromethane solutions of the
salts leads to nearly quantitave yields of ethoxyvinyl salts without
any further heating[120,121].
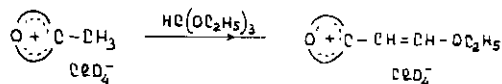
2-(β-Ethoxy)vinylpyrylium salts undergo hydrolysis with acids and
bases[118, 120].
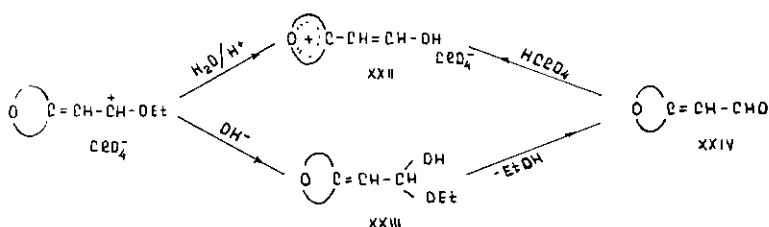
In both cases, the attack of nucleophiles is directed at the
positively charged β-carbon atom of the ethoxyvinylpyrylium salt.
However, in the first case, the stabilization of addition product
XXIII by the removal of the alcohol molecule is accompanied with
the protonation leading to β-hydroxyvinylpyrylium salt XXII.
Pyranylideneacetaldehydes XXIV are highly liable to protonation
with acids resulting in compounds XXII.

Reactions of ethoxyvinylpyrylium salts with amines may follow
the two pathways[122].

path A

Path B

Scheme 11

The reaction direction depends on the basicity of the amine.
Thus, aromatic primary amines[118,122] react in the direction A,
whereas with amines of higher basicity (methylamine, ammonia)[122]
path B is realized. With aromatic amines, the reaction occurs on
mixing of equimolecular quantities of the reactions in acetic acid.
Diamines react with both their amino functions to give the bis-products
(path A).

Heating equimolecular quantities of methylpyrylium salts, ethyl
orthoformate and aromatic amine in acetic acid can be used as a
one-step route to β – arylaminovinylpyrylium salts[122]. Basic
hydrolysis of arylaminovinylpyrylium salts results in azomethines,
whereas the hydrolysis with acids leads to α,β-unsaturated aldehydes.

Secondary amines react with ethoxyvinylpyrylium salts in acetic
acid to yield mixed acetal acetates XXX[122]. This result seems to
depend on a much higher basicity of secondary amines compared with
their aromatic analogues and hence much lower concentrations of
the free amine than those of the acetate anion. As a result, the
attack of the acetate ion on the ethoxyvinylpyrylium β-carbon atom
is favoured. The reaction yields dialkylaminovinylpyrylium salts
XXVI in aprotic solvents.

The interaction of 2-β-ethoxyvinylpyrylium salts with methylamine
(path B) leads to the substitution of the pyrylium oxygen atom with
the nitrogen one coupled with the hydrolysis of the β-ethoxyvinyl
function to the β-hydroxyvinyl one. Aqueous alkali converts N-
methyl-2-(β-hydroxyvinyl)pyridinium salts XXIX to the aldehydes XXXI[112].
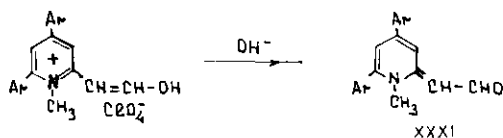
Reflux in acetic acid with ammonium acetate converts 2-(β-ethoxy-
vinyl)pyrylium salts to 2-(β-hydroxyvinyl)pyridines[122].
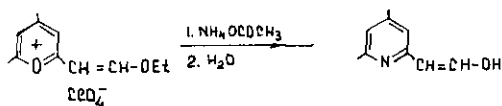
In the presence of pyridine[123] or sodium acetate[123,124].
2-(β-ethoxyvinyl)pyrylium salts react with compounds containing
activated methylene groups in refluxing acetic anhydride to produce
mero cyanines.
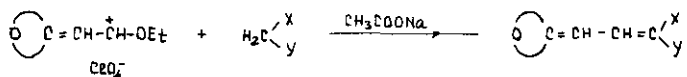
X,Y = COCH$_3$; CN; COC$_6$H$_5$; X = CN; C$_6$H$_4$NO$_2$; CN; COOC$_2$H$_5$ etc.

Melting together mero cyanines and ammonium acetate results in
the substitution of the heterocyclic oxygen atom with the nitrogen.[124]
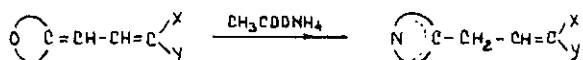
The action of perchloric aicd leads to the formation of pyrylium
salts containing the activated methylene group which easily and
quantitatively condenses with aromatic aldehydes.
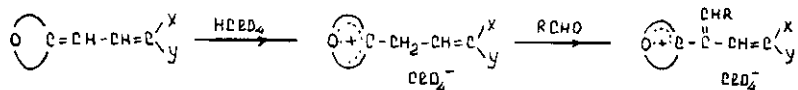
Dorofeenko and co-workers[125] have shown 2-β-ethoxyvinylpyrylium
and benzopyrylium salts to react with aromatic compounds in
refluxing acetic anhydride to yield styrylpyrylium salts.
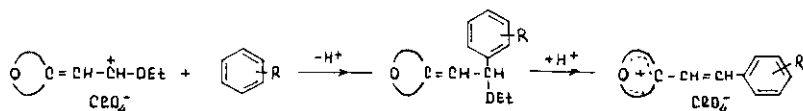
Monosubstituted benzenes (R = NR_2, OH, OR, Cl) give exclusively
para-derivatives. With indole, the attack occurs at the β-position.
In the case of nitrobenzene, the reaction involves the metha position
of the benzene nucleus which demonstrates an exclusively high re-
activity of the 2- and 4-(β-ethoxyvinyl)pyrylium β-carbon atom.

A one-step preparation of styrylpyrylium salts can be achieved
by refluxing acetic anhydride solutions containing methylpyrylium
salts, ethyl orthoformate and aromatic compounds. The yields are
rather high, so that the procedure does not require the isolation of
the intermediate β-ethoxyvinyl derivatives.

2- and 4-β-Ethoxyvinylpyrylium salts react with phenylmagnesium
bromide; the nucleophile attacks the ethoxyvinylpyrylium β-carbon
atom. The reaction products were converted to styrylpyrylium salts
on the treatment with perchloric acid[124,126].
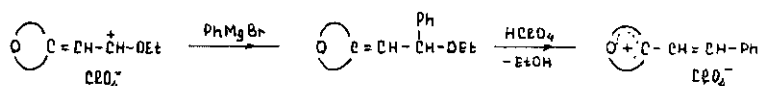
In the case of alkyl- and benzylmagnesium bromides, the resulting
salts are highly labile and their isolation is hardly possible.

The addition of aromatic and aliphatic nitriles occurs at the
β-carbon atom of 2- and 4-β-ethoxyvinylpyrylium salts. Hydrolysis

In the case of alkyl- and benzylmagnesium bromides, the resulting
salts are highly labile and their isolation is hardly possible.

The addition of aromatic and aliphatic nitriles occurs at the
β-carbon atom of 2- and 4-β-ethoxyvinylpyrylium salts. Hydrolysis
of the resulting nitrilium salts with acids gives β-hydroxyvinyl
derivatives and carboxylic acids[124,126].
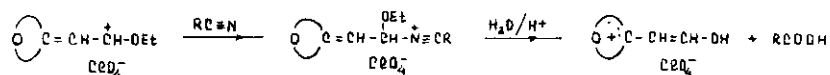
Ethoxyvinylpyrylium salts condense with salts of various methyl-
substituted heterocycles in refluxing acetic anhydride[121] or
pyridine[127] to yield symmetric and asymmetric cyanine dyes.
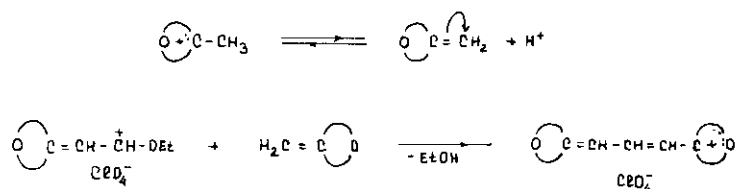
2-(β-Ethoxyvinyl)pyrylium salts in dioxane solutions add bromine
at the C = C double bond under the action of equimolecular quantities
of Br_2[121].
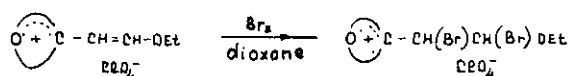
Heating 2- and 4-β-ethoxyvinylpyrylium salts with ethyl vinyl
ether in acetic acid affords 2-(β-ethoxydivinyl)pyrylium salts[128].
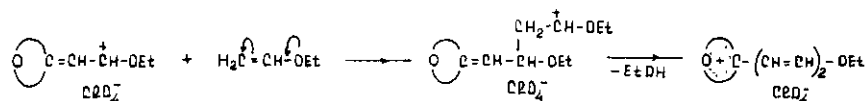
Ethoxydivinylpyrylium salts react with aromatic amines, reactive
aromatic compounds and compounds bearing activated methylene groups
to yield aminodivinylpyrylium salts, 1,4-disubstituted butadienes and
tetramethine mero cyanines, respectively. However, their reactivity
is somewhat lower than that of 2-(β-ethoxyvinyl)pyrylium salts.
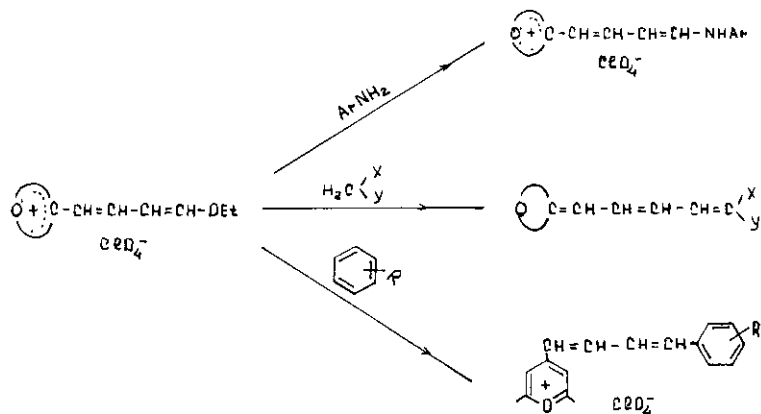
5. Other Reactions of Methylpyrylium Salts

Van Allan and Reynolds[85,129] observed methylflavylium salts to undergo autocondensation on heating in pyridine solution to yield the dimer XXXII. The reaction was supposed to follow the radical pathway represented in Scheme 12.
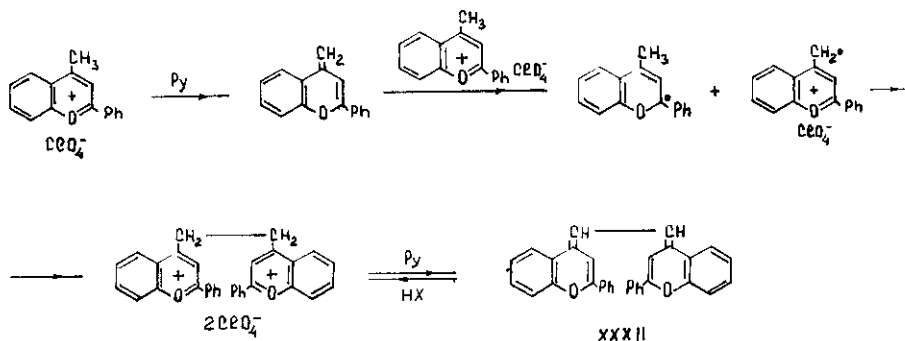
Scheme 12

Methylflavylium salt polymerized to compound XXXIII is allowed to stay in acetonitrile solution for a long period of time[111]. The mechanism of this conversion is not clear.

XXXIII
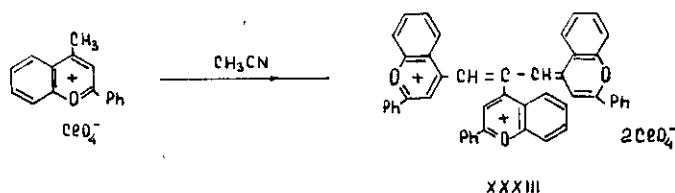
When heated in acetic acid/pyridine solution, methylpyrylium salts condense with flavylium salts to compounds XXXIV[130]. The reaction is believed to develop as follows.
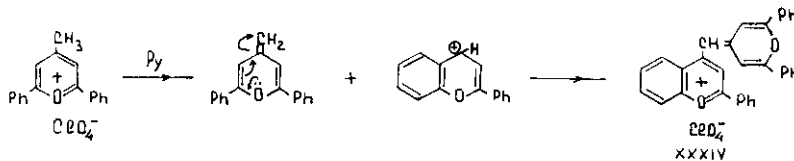
Pyrylium methylene groups readily enter the Michael condensations yielding 1,5-diketones XXXV. The cyclization of the latter via the hydride cleavage gives bis-pyrylium salts[112].
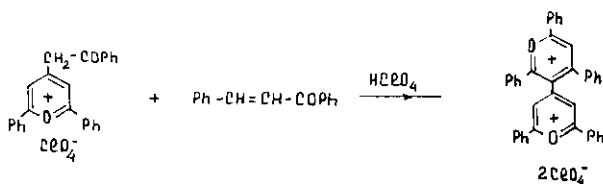
Acyl chlorides react with pyrylium methyl groups to produce pyranine XXXVI[18].
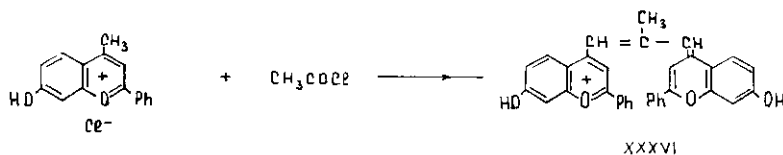
Van Allan[131] reported the isolation of benzylidenepyran derivatives by the reaction of 2,6-di-tert-butyl-4-methylpyrylium perchlorate with 2,4-dinitrochlorobenzene.

2,4,6-Trimethyl and 2-methyl-4,6-diphenylpyrylium perchlorates, amines and formaldehyde undergo the Mannich reaction in refluxing methanol or acetic acid to yield aminoethylpyrylium salts[132].

$$R = CH_3 , C_6H_5$$

In the first reports on the isonitrosation of alkylpyrylium salts with sodium nitrite or isoamyl nitrite[12,41,133] the products were supposed to have the isonitroso structure , however, this supposed ion was not rigorously verified.

Recently, 2,4-diaryl-6-methylpyrylium salt has been shown to give true nitroso compounds under the action of isoamyl nitrite[134]. This conclusion is based on the UV spectral data and chemical transformation of the product.

One of the possible mechanism of the isonitrosation reaction is s follows.

Scheme 13

The reaction of methylenepyran XXXVII and amyl nitrite[12] lends
support to the idea of the intermediate formation of a methylene base.
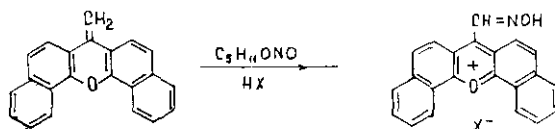
Fuming nitric acid in glacial acetic acid[134] as well as tetranitro-
methane in pyridine[12] causes nitration of methyl groups of pyrylium
salts.
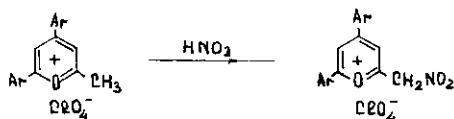
When heated in acetic acid in the presence of sodium acetate,
methylpyrylium salts react with isonitroso compounds to give
asymmetrical monomethine cyanines via the removal of hydrogen
cyanide[127,135].
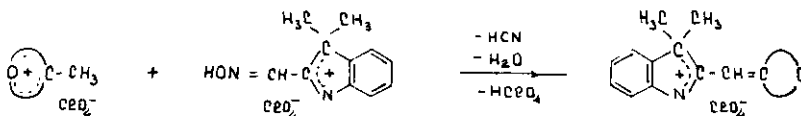
Khromov-Borisov and Gavrilova[108,136] showed that pyrylium salts
containing activated methyl groups readily undergo the diazo-coupling
reaction.

R= H, NO$_2$
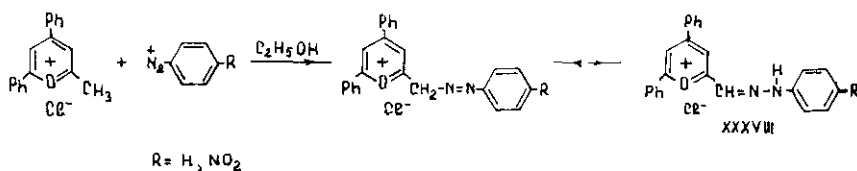
To show the validity of structure XXXVIII proposed[136] compound
XXXVIII was converted to the N-methylpyridinium salt which was
also synthesized otherwise.
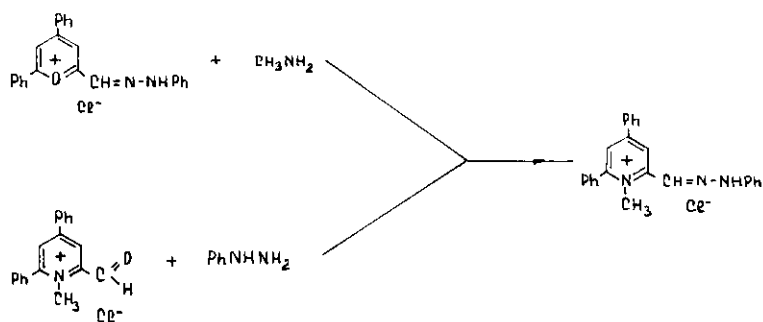
α-Methylpyrylium salts react with secondary amines under mild conditions to give N,N-dialkylanilines, via the cleavage of the ring followed by the cyclization of the intermediate dialkylaminoketones (XXXIX)[137-139].
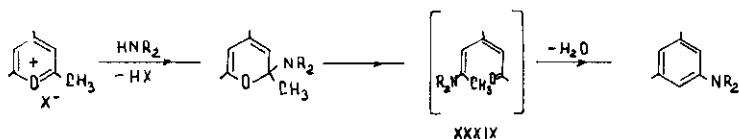
2,4,6-Trisubstituted pyrylium[140-146], thienopyrylium[147,148], benzofuranopyrylium[5], selenopyrylium[149,150], 2-benzopyrylium[151] salts containing α-methyl groups convert to phenols under the action of alkali.

The deuterated phenol was also obtained in this way[152].

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