Russian Chemical Reviews, **51** (5), 1982

Translated from *Uspekhi Khimii*, **51** 817-847 (1982)

U.D.C. 547.812

Reactions of Pyrylium Salts with Nitrogen-containing Nucleophiles

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New data on reactions of pyrylium salts with nitrogen-containing nucleophiles, occurring both with retention of the pyrylium ring and with recyclisation, are considered. The extensive possibilities for the employment of pyrylium salts in the synthesis of many functional compounds of the aliphatic and aromatic series and of different nitrogen- and oxygen-containing three-, five-, six-, and seven-membered heterocycles, including condensed heterocycles, are demonstrated.
The bibliography includes 184 references.

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I. INTRODUCTION

The vigorous development of the chemistry of pyrylium salts observed in recent years is associated not only with the enormous theoretical interest in the reactions of the carboxonium cation but also with the possibility of using such salts for the synthesis of many aliphatic, aromatic, and heterocyclic compounds, which sometimes cannot be obtained by other procedures. In this sense, the cyclisation reactions of pyrylium salts under the influence of nitrogen-containing nucleophiles are of particular interest. They lead to compounds among which effective biologically active substances, dyes, metal corrosion inhibitors, emulsifying agents, etc. have been found[1,2].

Pyrylium salts, which have a positive charge in the heterocycle, are exceptionally reactive to nucleophiles. The presence of a sextet of π electrons is responsible for the aromatic properties of the pyrylium cation. However, the electronegative oxygen heteroatom promotes a non-uniform electron density distribution in the ring. A high positive charge is therefore concentrated at the 2-, 4-, and 6-carbon atoms, whilst the charge at C(3) and C(5) atoms is quite insignificant, or these atoms are even negatively charged[3,4].

The first stage in the reaction of pyrylium salts with nucleophiles is the addition of the nucleophiles to C(2) or more rarely to C(4). The attack on the 2-position in the pyrylium ring is accompanied by ring opening and recyclisation (the S_NANRORC mechanism). The structure of the reaction product depends on the nature of the nucleophile, the substituents in the pyrylium ring, and the process conditions.

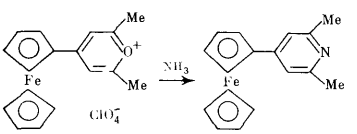
The reactions of pyrylium salts with ammonia, ammonium carbonate and acetate, and certain amines have been partly considered in other reviews[5-8] covering the literature up to 1972. The review of Plas and Streef[9], which deals with the recyclisation of various heterocycles, also presents several examples of the above reactions.

In the present review an attempt has been made to survey the extensive experimental data on the reactions of pyrylium salts with a wide variety of nitrogen-containing nucleophiles, which have accumulated in recent years (up to 1980 inclusive). Some attention has also been devoted to studies published up to 1972 but not included in the reviews quoted above.

Apart from the reactions of monocyclic pyrylium structures, the behaviour of the benzo- and heterocyclic analogues has also been considered, which we believe makes it possible to assess more fully the problem of the reactivity of heteroaromatic cations with *N*-nucleophiles in general.

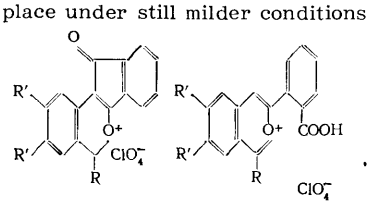
II. INTERACTION OF PYRYLIUM SALTS WITH AMMONIA AND THE SIMPLEST AMINES

In recent years the interaction of pyrylium salts with ammonia led to the synthesis of new compounds of the pyridine series otherwise difficult to obtain[10-23], for example:

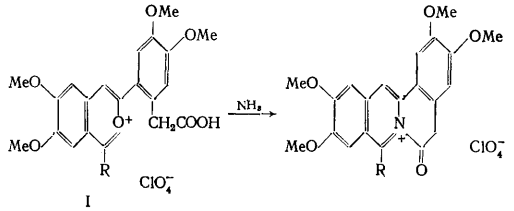


2-Benzopyrylium as well as pyrylium salts condensed with N-, O-, S-, and Se-containing heterocycles react with ammonia to give respectively isoquinoline bases of pyridines condensed with heterocycles. Hitherto unknown isoquinolines or isoquinolines difficult to obtain[24,25], pyridines with condensed cycloalkene rings[26-32] and steroids[33], disteroidopyridines[34], indolo[2,3-*c*]pyridines[35], benzofuro[3,2-*c*]pyridines[36,37], thionaphtheno[2,3-*c*]pyridine[38], selenopheno[3,2-*c*]pyridines[39,40], selenopheno[2,3-*c*]pyridines[41,42], and pyrido[2,3-*d*]pyrimidines[43] have been obtained by this method.

1-Alkyl(aryl)-3,4-diaryl-2-benzopyrylium salts are converted by ammonia into isoquinolines more readily[44] than the 1-alkyl(aryl)-3-aryl-substituted derivatives[45]. The exchange of the ring oxygen atom for nitrogen in 3-aryl-substituted 2-benzopyrylium salts without a substituent in the 1-position[46] and in salts with the electron-accepting carbonyl group[30] takes place under still milder conditions:

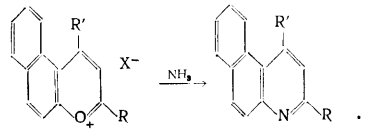


When the salts (I) interact with ammonia, the replacement of the oxygen hetero-atom by nitrogen is accompanied by the formation of a new ring[47]:



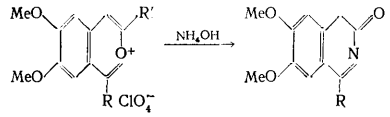
I

1-Benzopyrylium and xanthylium salts cannot be converted into quinolines and acridines by treatment with ammonia[48], but naphtho[*b*]pyrylium salts have been converted into benzoquinoline derivatives in satisfactory yield by reaction with ammonia[49]:



The reactions of 5,6,7,8-tetrahydrochromylium and symmetrical octahydroxanthylium salts with ammonia, leading to 5,6,7,8-tetrahydroquinolines and octahydroacridines, take place under mild conditions[27].

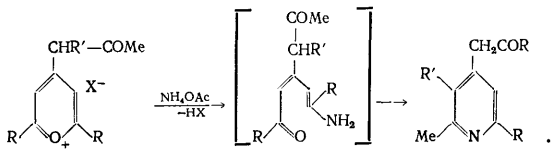
The reaction of 2-benzopyrylium salts containing the 3-OCH_3 group with aqueous ammonia results in the hydrolysis of the intermediate ether and subsequent cyclisation to 3-oxo-4*H*-isoquinoline[50]:



R=Alk, R′=OMe, $PhCOCH_2O$, EtCOO, R″CONH .

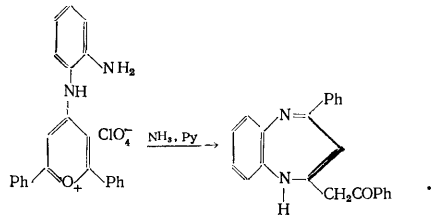
Isoquinolones are formed in high yields also in the reactions of 1-alkyl-3-phenacyloxy-[51] and 1-alkyl-3-acylamino-2-benzopyrylium salts[52] with ammonia. Similarly 1-alkyl-3-methoxy-5,6,7,8-tetrahydro-2-benzopyrylium salts are converted by reaction with ammonia into 1-alkyl-5,6,7,8-tetrahydroquinolones[53]. Pyrylium salts with a free 4-position react with ammonia to form 2,6-disubstituted pyridines[54]. 2-Ethoxyvinylpyrylium salts recyclise to pyridines on reaction with ammonia[55] and the ethoxyvinyl group is simultaneously hydrolysed to the β-hydroxyvinyl group.

The conversion of 4-acetonylpyrylium salt into pyridine with participation of the keto-group of the substituent in the intramolecular cyclisation of the intermediate enamine is of interest[56]:

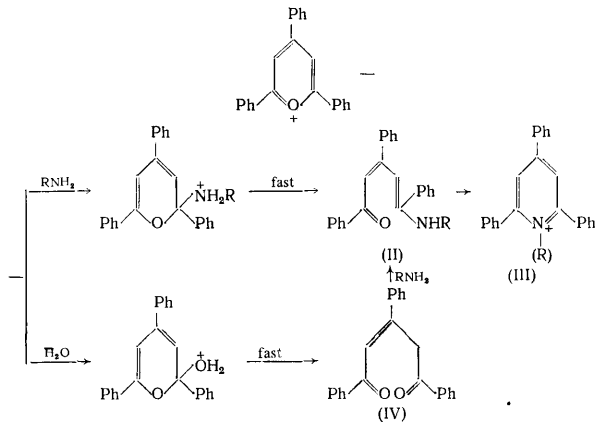


The presence of the electron-donating amino-group in 4-*p*-aminophenylpyrylium salts diminishes somewhat the electrophilicity of the pyrylium ring, but the reaction of these salts with ammonia take place more readily and leads to pyridines[57]. The reaction of *N*-substituted aminopyrylium salts with ammonia proceeds under more severe conditions[19,58]. As a consequence of a still greater delocalisation of the positive charge in the vinylogues of aminopyrylium salts, the ring oxygen heteroatom is not substituted by nitrogen[55].

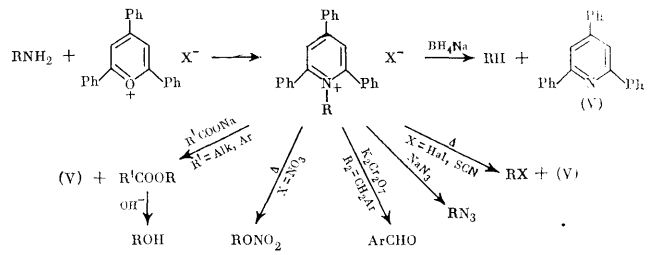
4-(*o*-Aminoanilino)-2,6-diphenylpyrylium perchlorate remains unchanged on being refluxed with ammonium acetate in acetic acid, but the reaction of the salt with ammonia in pyridine leads to its conversion into substituted 1*H*-benzo-1,5-diazepine[59]:



The reactions of arylpyrylium salts with aliphatic amines proceed under mild conditions and with high yields of *N*-alkylpyridinium salts[60,61]. Recent kinetic studies on this reaction by ^{13}C NMR and ultraviolet spectroscopy showed that the rate-limiting stage is the closure of the pyridine ring (II) → (III), which can be catalysed by acids[60,62]:

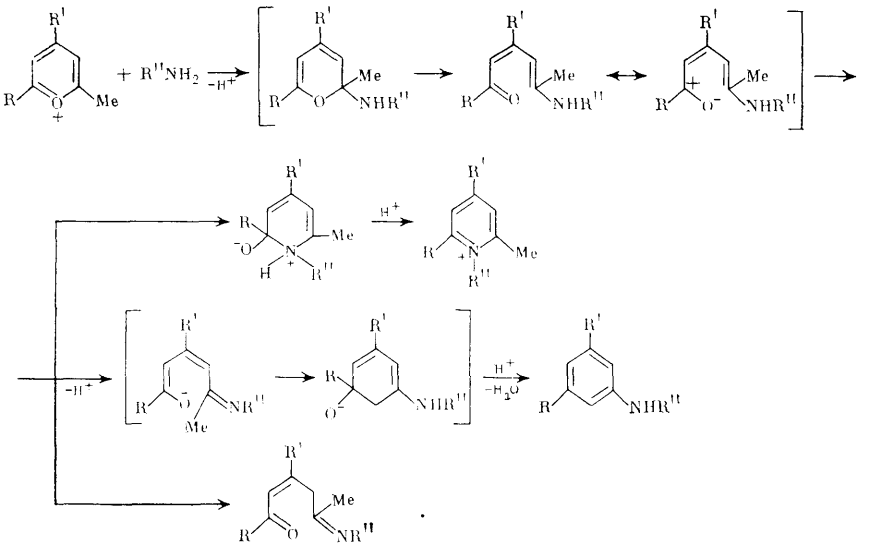


It has also been shown that, together with the main reaction, the diketone (IV) is formed under the influence of traces of water. The diketone (IV) reacts with the amine, giving rise to the pyridinium salt (III), possibly via the aminoketone (II)[60,62]:



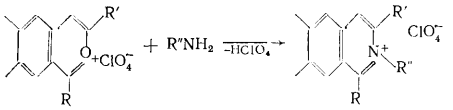
The salts (III) readily split off 2,4,6-triphenylpyridine on being subjected to mild pyrolysis or on treatment with nucleophiles, which makes it possible to employ the reaction of primary amines with pyrylium salts as an intermediate stage in the conversion of amines into hydrocarbons, ethers, alcohols, alkyl halides, thiocyanates, aldehydes, azides, and other derivatives[60].

Substituted xylidines may be formed in the reaction of 2-methylpyrylium salts with aliphatic amines together with the conversion into pyridinium salts[63]:

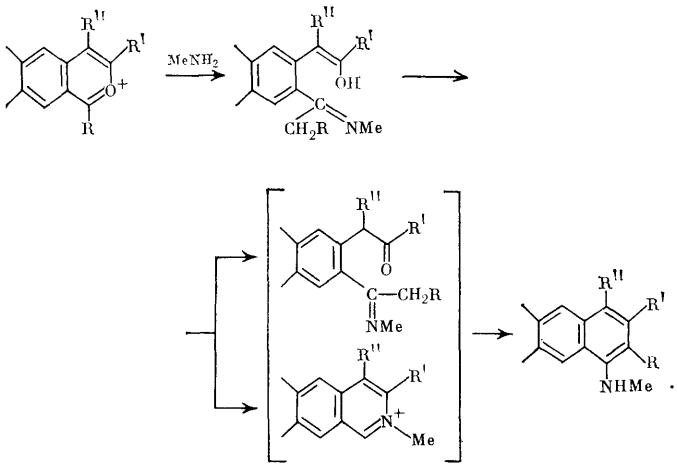


The ratio of the amounts of pyridinium salts and xylidines depends on the nature of the amine. In the case of aliphatic amines and benzylamines the predominant product is pyridinium salts. Cyclohexylamine reacts with 2,4,6-trimethylpyrylium salts to form xylidine, while amines with C_2–C_5 aliphatic groups form xylidines in yields of 30–40%. The interaction with t-butylamine stops at the stage involving the formation of *N*-butylketodienamine, which is the third possible reaction pathway[63].

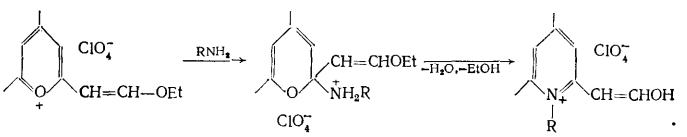
The reaction of 2-benzopyrylium salts with primary amines results in the formation of isoquinolinium salts. Nucleophilic attack by the amine is directed to the most electron-deficient C(1) atom with formation of benzo-1*H*-pyran, which recyclises via an enamine to an isoquinolinium salt[64,65]:



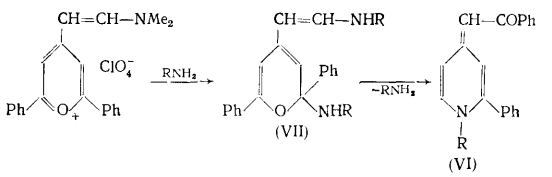
1-Alkyl-3-aryl-substituted 2-benzopyrylium salts, which form α-naphthylamines in the presence of an excess of methylamine, constitute an exception[66,67]. In this case either the second possible version of the cyclisation of the intermediate enamine takes place or the isoquinolinium salt formed recyclises under the influence of the excess amine via the Kost–Sagitullin mechanism[68]:



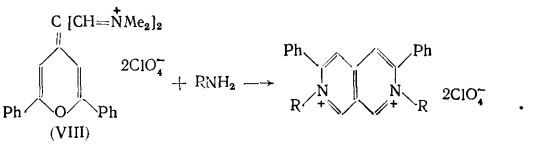
4-Methoxy-2,6-dimethylpyrylium salt reacts with methylamine to form a 4-methoxy- or 4-methylamino-pyridinium salt, depending on the reactant ratio[69]. 2-Benzopyrylium salts with the 3-methoxy-group react with an alcoholic solution of methylamine to form quaternary *N*-methylisoquinolinium salts[50]. Ethoxyvinylpyrylium salts react with aliphatic amines via the mechanism[55]



4-Dimethylaminovinyl-2,6-diphenylpyrylium perchlorate interacts with primary aliphatic amines to form pyridines (VI), which is a result of the recyclisation of the intermediate aminovinylpyran (VII)[70]:

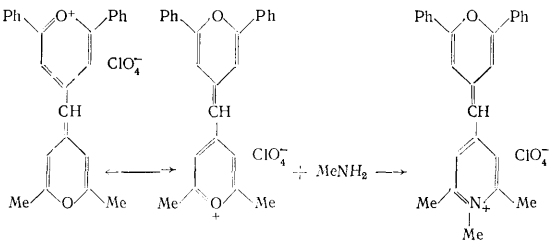


The bisiminium salt (VIII) leads to diquaternised copyrines in an analogous reaction[70]:

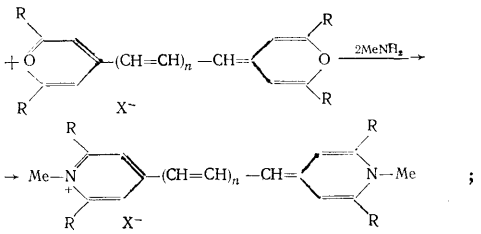


The positive charge in pyrylocyanines is delocalised over the entire mesomeric cation, which diminishes their electrophilicity. Nevertheless, even in alcohol the reaction with

ethylamine leads to pyridopyrylocyanine and in the asymmetric cyanine (IX) the oxygen in the dimethylpyrylium ring is the first to be substituted[71]:



The substitution of the second oxygen atom by nitrogen does not occur in methanol[72,73]. In an aprotic solvent—dimethylformamide (DMF)—it is possible to obtain symmetrical tetramethyl(phenyl)pyrido-derivatives of mono-, tri-, and penta-methinecyanines[71]:

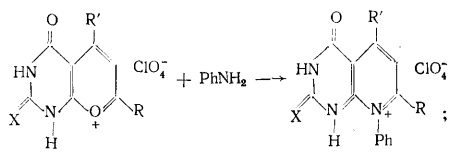


n=0, 1, 2; R=Me, Ph .

Isopropylcyanines exchange only the oxygen heteroatom for the methylamino-group in DMF, while t-butylcyanine does not react with methylamine at all[74].

The conversion of pyrylium and 2-benzopyrylium salts under the influence of aromatic amines into the corresponding *N*-arylpyridinium and isoquinolinium salts has been thoroughly investigated[64,65]. Analogously to their reaction with ammonia, chromylium and xanthylium salts are not converted into quinolinium and acridinium derivatives on reaction with anilines. Nucleophilic attack on the xanthylium salt is directed to the 9-position, which results in the formation of aminoarylxanthenes[48].

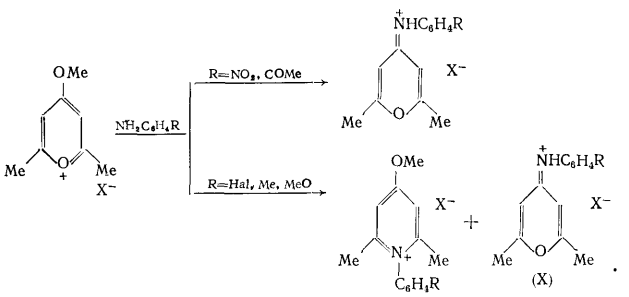
Naphtho[1,2-*c*]- and naphtho[2,1-*c*]-pyrylium salts were made to react with *p*-aminophenol, which yielded benzoquinolinium salts[49]. In contrast to 1-benzopyrylium salts, the condensed pyrylia[2,3-*d*]pyrimidine systems react with aniline to form *N*-phenylpyridinium salts[43]:



X=O, S .

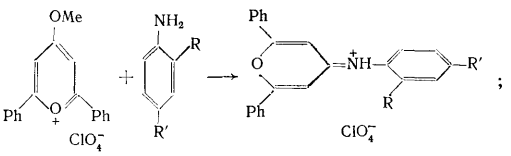
5,6,7,8-Tetrahydrochromylium and symmetrical octahydroxanthylium salts give rise to 5,6,7,8-tetrahydroquinolinium and symmetrical octahydroacridinium salts on treatment with primary amines[75,76].

The reaction of 4-methoxy-2,6-dimethylpyrylium salts with an equimolar amount of *p*-substituted anilines results in the formation of an iminopyran salt (X) together with the 4-methoxypyridinium salt[77]:



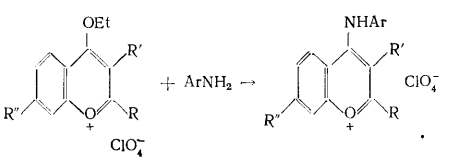
Anilines with electron-accepting substituents form only the products resulting from the attack on the 4-position of the pyrylium ring, i.e. an iminium salt (X). More basic amines with electron-donating substituents attack preferentially the 2-position of the pyrylium cation forming a greater amount of the alkoxypyridinium salt the more pronounced the electron-donating effect of the substituent[77].

It is noteworthy that 4-methoxy-2,6-diphenylpyrylium perchlorate is converted exclusively into pyran iminium salts in the reaction with anilines[59]:

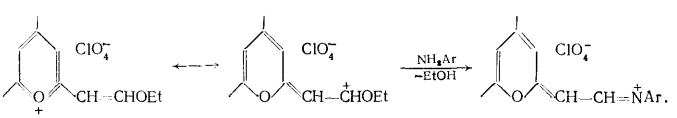


R=H, NH_2, OMe, R′=H; R=H, R′=NH_2, NMe_2, NHCOMe .

The reaction of 4-ethoxychromylium salts with primary amines proceeds analogously[78,79]:



Ethoxyvinylpyrylium salts react with aromatic amines, retaining the pyran ring[55]:

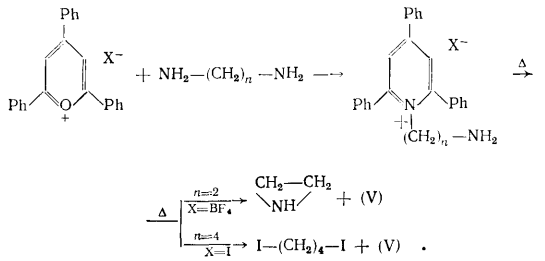


p-Aminophenylpyrylium salts react with aniline only on refluxing in DMF[57].

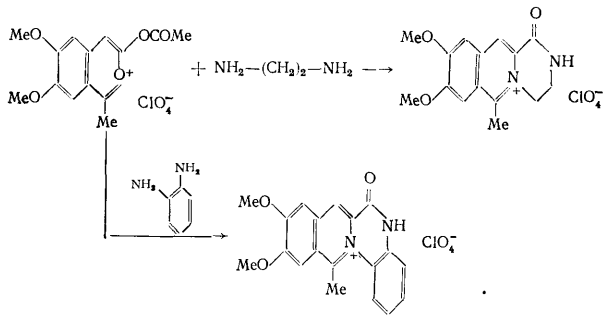
The reactions of pyrylium and 2-benzopyrylium salts with aliphatic and aromatic diamines in molar proportions of 2:1 give rise to bispyridinium salts[65,80-82]. The interaction of pyrylium perchlorate with an equimolar amount of an arylenediamine results in the formation of *N*-aminoarylpyridinium salts[83,84], which react with pyrylium perchlorates to form *m*- or *p*-arylenebispyridinium salts[84] and it is possible to obtain by this procedure compounds with pyridine rings substituted in different ways. *o*-Phenylenediamine reacts with pyrylium salts only via one amino-group, probably owing to steric hindrance. *N*-(*o*-Aminoaryl)pyridinium salts do not form bispyridinium derivatives probably for the same reason[84].

The reactions of equimolar amounts of 2,4,6-triphenylpyrylium salts and aliphatic diamines lead to *N*-aminoalkyl-2,4,6-triphenylpyridinium salts, which have been suggested

for the preparative synthesis of aziridine[85] and di-iodobutane[86] via their pyrolytic decomposition:

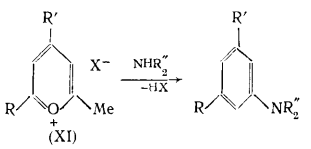


It is of interest that 2-benzopyrylium salts with the 3-methoxycarbonyl group react with certain diamines via two reaction centres[87]:



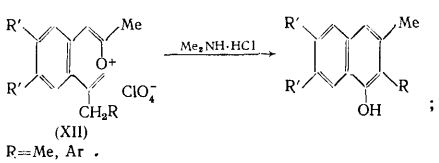
The same pyrylium salts react with *p*-phenylenediamine or 1,8-diaminonaphthalene and are converted into *N*-aminoaryl-substituted quaternary isoquinolinium salts[87].

Pyrylium salts having a 2-methyl or methylene group [compounds (XI)] react with secondary amines and are converted under mild conditions into *N*-substituted anilines[88-90]:



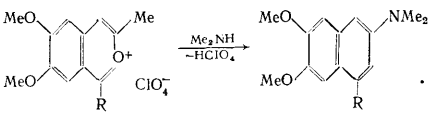
The basicity of the amine plays a significant role in this process. Thus the reaction with highly basic dialkylamines takes place vigorously without heating[88,89]. The reaction of the less basic indoline with the salt (XI, X = ClO_4^-, R = R′ = 4-$MeOC_6H_4$) does not result in the formation of the corresponding *N*-arylindoline[89].

1-Methyl-2-benzopyrylium salts react with cyclic and aliphatic secondary amines to form dialkylaminonaphthalenes[65]. An anomalous reaction of 1-ethyl(benzyl)-substituted 2-benzopyrylium salts (XII) with dimethylamine in ethanol, resulting in the formation of α-naphthols, was discovered recently[91]:



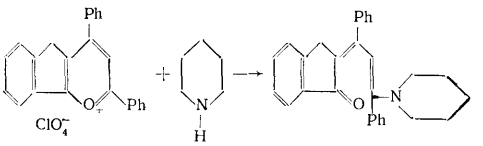
The same reaction takes place when the perchlorate (XII) is acted upon by alkali[92], i.e. the dimethylammonium salt has a catalytic effect on the recyclisation of the 2-benzopyrylium cation with participation of the water present in the alcohol.

The perchlorates (XII, R = H or Me) react with gaseous dimethylamine and recyclise to tertiary β-naphthylamines, which can be accounted for only by the initial attack of the nucleophile on the C(3) position[93]:

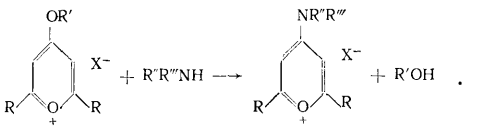


Thieno- and seleno-[2,3-c]pyrylium salts react analogously with dimethylamine[94].

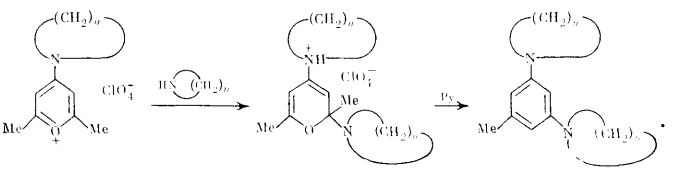
Arylpyrylium salts without an alkyl group in the 2-position are quantitatively converted into dialkylaminoketones on treatment with two equivalents of a secondary aliphatic amine[32,62], for example:



2- or 4-Alkoxypyrylium salts react with secondary aliphatic and heterocyclic amines, retaining the pyrylium ring[58,69,88,95,96]:

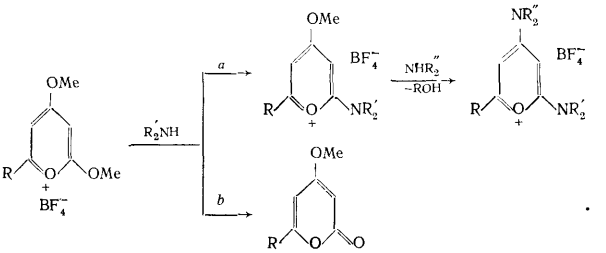


An excess of the amine as well as an increase of temperature promote the formation of the product of the addition of two moles of the secondary amine, which, on heating in pyridine, recyclises to an *m*-diaminobenzene derivative[58]:



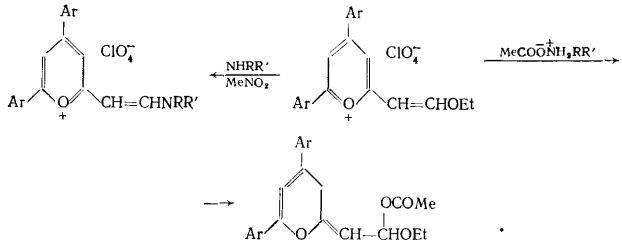
2-Phenylpyrylium salts do not form similar bisadducts.

The reactions of 2,4-dimethoxypyrylium salts with secondary amines proceeds via two pathways: the main pathway involves nucleophilic substitution of the C(2) atom (pathway *a*), while the minor pathway involves the methylation of the amine, i.e. the attack on and dissociation of the O–CH_3 bond with formation of a quaternary ammonium salt and an α-pyrone (pathway *b*)[97]:

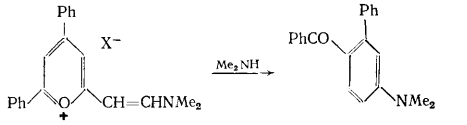


The reaction of an excess of a secondary amine results in the conversion of a 2-amino-4-ethoxypyrylium salt into a 2,4-diaminopyrylium salt[98].

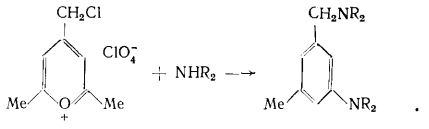
2-Ethoxyvinylpyrylium salts react with secondary amines to form either aminovinylpyrylium salts or acetal-acylals, depending on the solvent employed[55]:



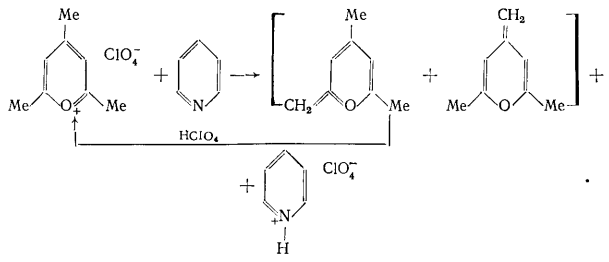
The reaction of aminovinylpyrylium salts with secondary amines can involve the substitution of one amino-group by the other[70]. 2-Dimethylaminovinyl-4,6-diphenylpyrylium is converted into a benzoylaniline on reaction with dimethylamine[99]:



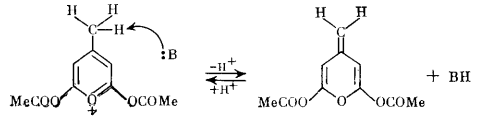
The halogen in 4-halogeno-2,6-diphenylpyrylium salts is readily substituted on reaction with secondary cyclic and alicyclic amines, various 4-dialkylaminopyrylium perchlorates being formed[100]. 4-Chloromethyl-2,6-dimethylpyrylium perchlorate reacts with secondary amines both in the 2-position of the pyrylium ring and via the substituent in the methyl group, forming aromatic diamines[101]:



The reaction of 2,4,6-trimethylpyrylium perchlorate (TMPP) with triethylamine, pyridine, benzimidazoles, imidazoles, quinoline, and pyrazoles takes place with deprotonation of the methyl group of the pyrylium cation[102–104]:



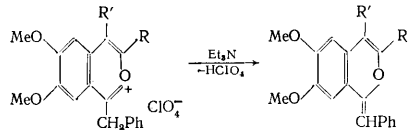
The study of the infrared spectra of the pyridinium perchlorates formed in the reaction with selectively 2- or 4-deuterated TMPP showed that the proton is split off from both the 2-CH_3 and 4-CH_3 groups[102]. The resulting methylenepyrans, which are extremely reactive, undergo further transformation into methylenepyran hexamers, whose structure could not be determined[103]. Comparatively stable methylenepyrans can be obtained only in the presence of effective electron-accepting substituents in the pyran ring. Thus a methylenepyran has been isolated and spectroscopically characterised in the reaction of a 2,6-dimethoxycarbonyl-4-methylpyrylium salt with pyridine[105]:



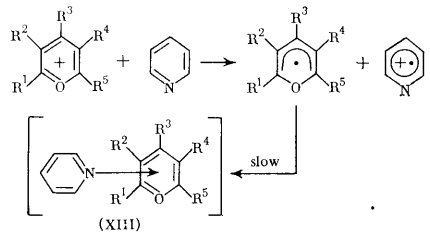
It is of interest that aniline acts on this salt similarly to pyridine.

The dimerisation of 4-methylflavylium perchlorate in pyridine is also believed[106,107] to proceed via the intermediate formation of methylenepyran.

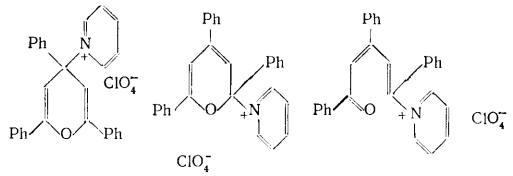
On treatment with triethylamine in an anhydrous medium, 1-benzyl-2-benzopyrylium salts give rise to stable benzylideneisochromenes[108]:



On dissolution in anhydrous pyridine, polyarylpyrylium salts generate pyranyl radicals[109], the EPR spectra of which are identical with those of the radicals formed on reduction of the corresponding pyrylium salts with zinc[110,111]:

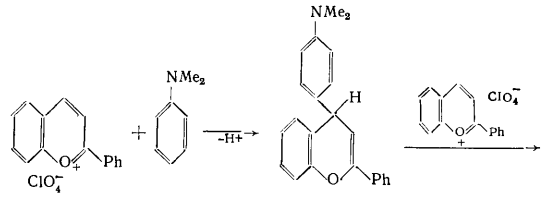


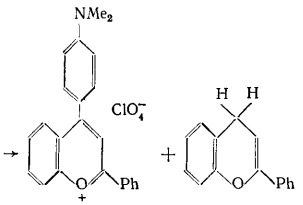
The pyranyl radicals react slowly with pyridine to form donor–acceptor complexes (XIII). It has been established that a small amount of products of the addition of pyridine to the 4- or 2-position of the pyrylium ring and an acyclic valence isomer of the latter are present in the pyridine solution of 2,4,6-triphenylpyrylium perchlorate (TPPP) in addition to the complex (XIII, $R^1 = R^3 = R^5 = Ph$; $R^2 = R^4 = H$)[112]:



It has been shown that TPPP forms charge-transfer complexes also with triphenylamine and its derivatives[113].

Pyrylium and 1-benzopyrylium salts with a free 2- or 4-position react with aryl-substituted tertiary amines and heterocyclic compounds having an excess of electrons to form aminoaryl or heteroaryl-pyrylium salts[15,114–116], for example compound (XIV):

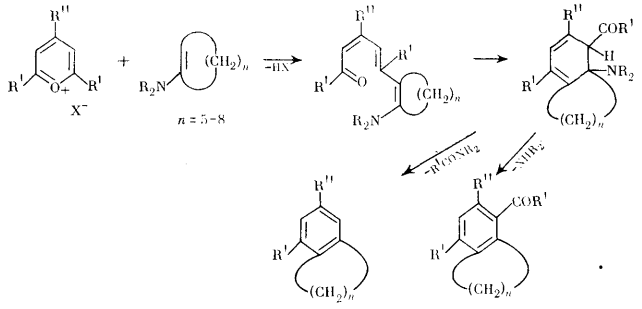




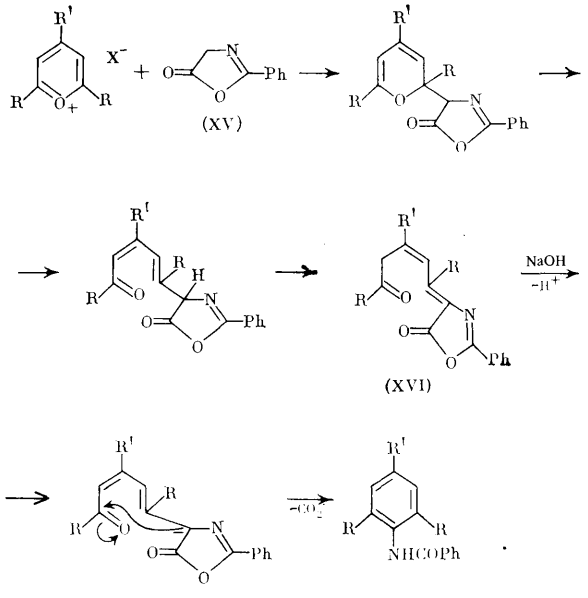
(XIV)

Heteroarylpyrylium salts are also formed when 2- and 4-methoxy-, 2- and 4-methylthio-, and 2- and 4-chloro-pyrylium salts react with nitrogen-containing heterocycles[100,116-121].

In the reactions of pyrylium salts with enamines containing a tertiary nitrogen atom (NR_2-pyrrolidinyl or NO_2-morpholinyl derivatives) the role of the amino-group split off in the process consists in increasing the nucleophilicity of the double bond[122]:



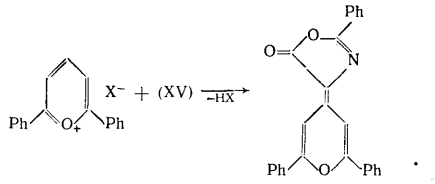
The interaction of the azlactone (XV) with 2,4,6-trisubstituted pyrylium salts proceeds via nucleophilic attack on the 2-position of the pyrylium ring, leading to the formation of the oxazolinones (XVI). After brief treatment with aqueous alkali, the latter are converted into *N*-benzoylanilines[123]:



(XV)

(XVI)

The interaction of compound (XV) with 2,6-diphenylpyrylium salts leads to pyranylideneoxazolinone[123]:

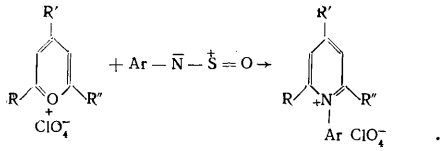


Pyranylidenethiazolinones have been obtained analogously[124].

Thus, nitrogen-containing non-aromatic heterocycles react with pyrylium salts via the most nucleophilic carbon atom.

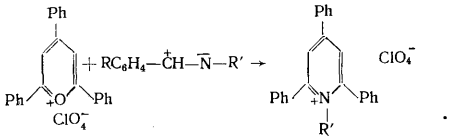
III. REACTIONS WITH COMPOUNDS CONTAINING THE S = N, C = N, AND N_3 GROUPS

The reaction of pyrylium salts with thionylanilines in DMF leads to *N*-arylpyridinium salts[125]. The author suggests that it begins with the addition of thionylaniline to the C(2) atom of the pyrylium ring with subsequent opening of the pyran ring via the intramolecular 1,2-cycloaddition and the elimination of the SO_2 molecule:

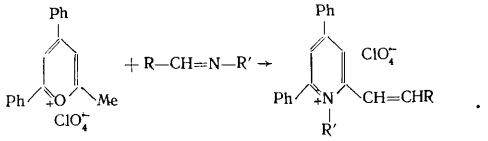


Since the reaction was carried out under conditions ruling out the hydrolysis of thionylanilines, the alternative reaction mechanism involving the hydrolysis of thionylaniline and the reaction of aniline with the pyrylium salt was excluded.

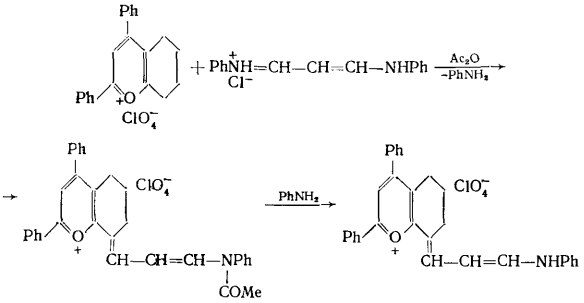
The interaction of TPPP with azomethines in DMF with formation of pyridinium salts[126,127] probably proceeds via a similar mechanism:



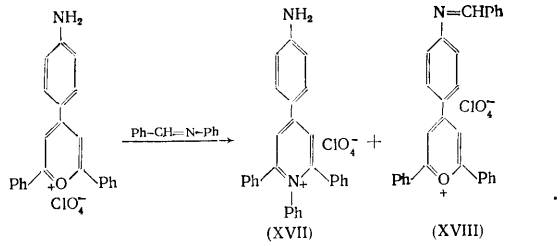
A pyrylium salt with a 2-methyl substituent gives rise to α-styrylpyridinium perchlorate[127]:



The reaction with the dianilide of malonic dialdehyde takes place via the methylene group in the 2-position of the pyrylium cation[128]:



The reaction of 4-(*p*-aminophenyl)pyrylium perchlorate with benzylideneaniline yields two salts—(XVII) and (XVIII)[57]. The reaction takes place preferentially in the 2-position of the initial perchlorate, resulting in the formation of pyridinium salts (XVII), while the benzaldehyde produces the azomethine (XVIII) on reaction with the initial salt[57]:

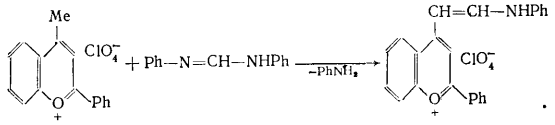


(XVII) (XVIII)

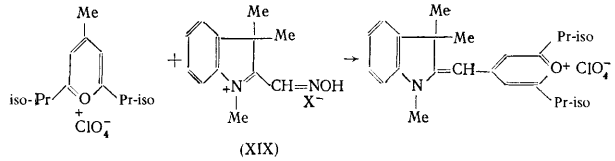
It has been shown separately that compound (XVII) does not react with benzaldehyde under these conditions.

The reaction of substituted 2-benzopyrylium salts with monobenzylidene-*o*-(or *p*-)phenylenediamines proceeds preferentially via the —CH=N— group and not the amino-group[84].

The reaction of 4-methylflavylium perchlorate with diphenylformamidine leads to an aminovinylpyrylium salt[129]:

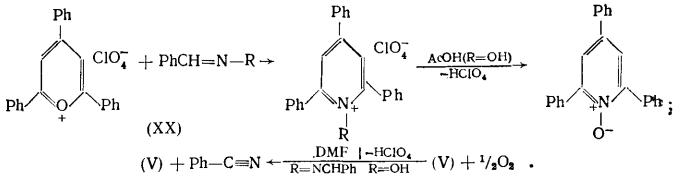


The reaction of 2,6-di-isopropyl-4-methylpyrylium perchlorate with the aldoxime (XIX) also involves the methyl group[72]:



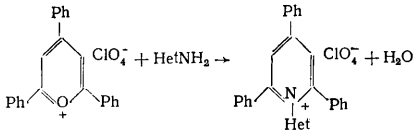
(XIX)

The reactions of TPPP with benzaldoxime (XX, R = OH), benzylidenephenylhydrazine (XX, R = —NHPh), and benzylideneazine (XX, R = —N=CHPh) have been investigated. The reaction with benzaldoxime in acetic acid yielded 2,4,6-triphenylpyridine *N*-oxide, while the reaction with benzylidenephenylhydrazine resulted in the formation of an *N*-anilinopyridinium salt[127]:



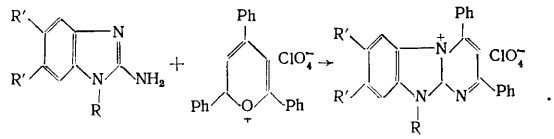
The pyridinium salts formed split off the pyridine (V) in boiling DMF. The reaction with benzylideneazine can be regarded as a method for the synthesis of benzonitrile.

In subsequent years it was found that the reaction of TPPP with heterocyclic amines leads to the formation of *N*-heteroarylpyridinium salts[103,130] (Het = heteroaryl):



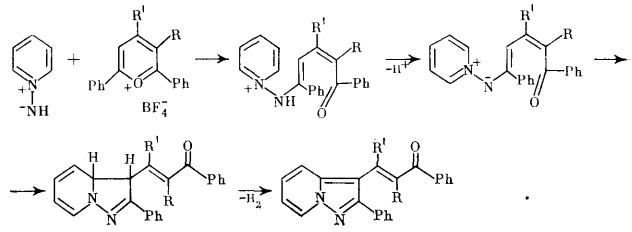
Analogous heteroarylpyridinium salts were obtained from 4-*p*-aminophenyl-2,6-diphenylpyrylium perchlorate[131] and TMPP[60,80,132,133]. However, only the amines whose basicity constants in acetonitrile are $pK_a \geq 5$ react with TMPP via this pathway[103]. The presence of the pyridine nitrogen atom in the heterocycle promotes the elimination of a proton from the methyl group of the pyrylium salt, which, as already mentioned, leads to the formation of a hexamer[103]. Heterocyclic amines in which the basicity of the amino-group is significantly reduced as a result of the significant contribution of the charged resonance form with the positive charge on the nitrogen of the amino-group interact via this pathway.

The condensation of *N*-aminoheterocycles with 2,4,6-substituted pyrylium salts yielded N—N linked heteroarylpyridinium salts[134]. Both nucleophilic centres of the aminoheterocycle molecule (the amino-group and the pyridine nitrogen atom) are involved in the reaction of TPPP with 1-alkyl-2-aminobenzimidazoles, which leads to the formation of pyrimido-[1,2-*a*]benzimidazolium salts[135,136]:

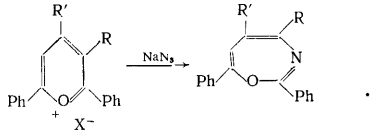


TPPP also forms the condensed pyrimido[1,2-*a*]naphthimidazolium system on reaction with 2-amino-3-benzylnaphtho-[1,2-*d*]imidazole[131,136]. However, the reaction of the above perchlorate with the azomethines of the above heterocyclic amines proceeds similarly to the reactions of benzylideneanilines, which leads to the formation of *N*-heteroarylpyridinium salts[127]. Thus it has been found that, if the heterocyclic amine does not form a quaternary pyridinium salt on reaction with TPPP, it can be obtained from the azomethine derived from the above amine.

The interaction of arylpyrylium salts with *N*-pyridinium imine proceeds via a non-standard pathway, where the 2-position of the pyridine reactant is involved in intramolecular 1,5-dipolar cyclisation. This results in the formation of a derivative of a pyrazolo[1,5-*a*]pyridine[137]:



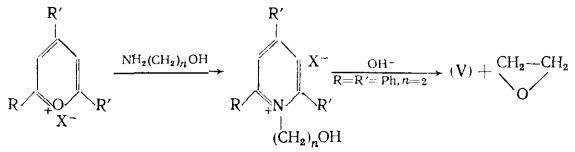
Monocyclic pyrylium salts recyclise to 1,3-oxazepines under the influence of sodium azide[138]:



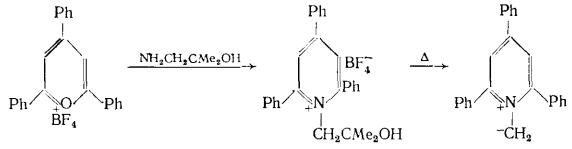
The reaction of 1-benzopyrylium perchlorates with sodium azide, leading to the formation of benzo[*f*]-1,3-oxazepines, proceeds analogously[139].

IV. INTERACTION WITH AMINES CONTAINING OTHER FUNCTIONAL GROUPS

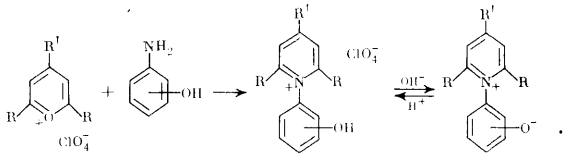
The interaction of pyrylium salts with aliphatic aminoalcohols yielded *N*-hydroxyalkylpyridinium salts[85,140,141]; some of their reactions have been investigated[85,140]:



A novel method has been discovered for the synthesis of 2,4,6-triphenylpyridinium methylide[85]:

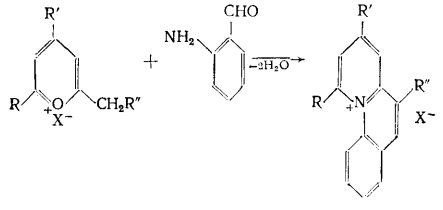


Pyrylium salts readily interact with *p*-, *m*- and *o*-aminophenols and their derivatives with the nitro-group in the *m*-position relative to NH_2, forming 1-hydroxyarylpyridinium derivatives, which are deprotonated on treatment with alkali to O^-–N^+-pyridinium betaines[142,143]:



The symmetrical octahydroxanthylium perchlorate is readily converted into *N*-substituted octahydroacridinium salts by reaction with *o*-, *m*- and *p*-aminophenols and ethanolamine[76].

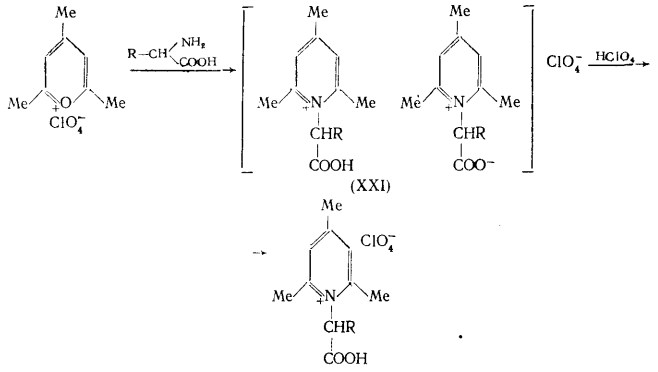
Both functional groups of *o*-aminobenzaldehyde are utilised in its reaction with 2-methyl(or methylene)-substituted pyrylium salts and derivatives of the condensed benzo[*c*]-quinolizinium system were obtained by simple single-stage synthesis[144]:



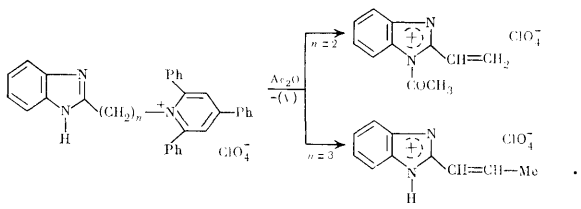
The reaction of pyrylium salts with aromatic aminoacids proceeds with formation of *N*-carboxyphenylpyridinium derivatives[130,145], which are deprotonated by ion-exchange resins, forming stable compounds with a zwitterionic structure[130].

The ethyl esters of glycine, phenylalanine, and glycylglycine readily react with TMPP, TPPP, and 5,6,7,8-tetrahydrobenzopyrylium and *sym*-octahydroxanthylium perchlorates to form *N*-alkoxycarbonyl derivatives of quaternary pyridinium, tetrahydroquinolinium, and octahydroacridinium salts[146,147].

The condensation of TMPP with α-aminoacids and peptides proceeds under less severe conditions than the condensation with their esters, giving rise to the dimeric products (XXI). On treatment with $HClO_4$, the latter are converted into pyridinium salts[145,148]:



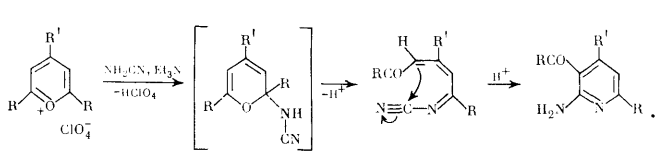
It has been shown that the reaction of TPPP with α-aminoacids does not give rise to condensation products[81]. The interaction of TMPP and TPPP with β-alanine and γ-aminobutyric acid takes place readily, resulting in the formation of the corresponding carboxypyridinium perchlorates. By reaction with *o*-phenylenediamine, the latter were converted into *N*-benzimidazolylalkylpyridinium salts, which underwent thermal decomposition on refluxing in acetic anhydride[81]:



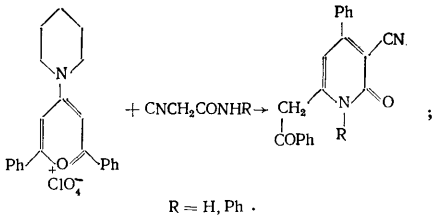
These reactions can be regarded as a simple method of synthesising 2-alkenylbenzimidazoles.

Diaminomonocarboxylic acids (lysine and ornithine) interact with TMPP and TPPP via the ε- or δ-amino-group, forming aminoacids with a pyridinium substituent[149]. On the other hand, pyrylium salts do not react with aminodicarboxylic acids (aspartic and glutamic). The above studies have demonstrated the possibility, in principle, of reactions of pyrylium salts with the free amino-groups of proteins; it has been suggested that the mutagenic action of TMPP is based on this factor[150,151]. The same pyrylium salt has been used as a selective reagent for the chemical modification of α-chymotrypsin[152].

2,4,6-Triarylpyrylium salts interact smoothly with cyanamides in the presence of triethylamine, forming 2-amino-3-aroylpyridines[153]. The reaction with cyanamide belongs to the class of rare reactions in the chemistry of pyrylium salts in which cyanamide behaves initially as the nucleophile and then as the electrophile:

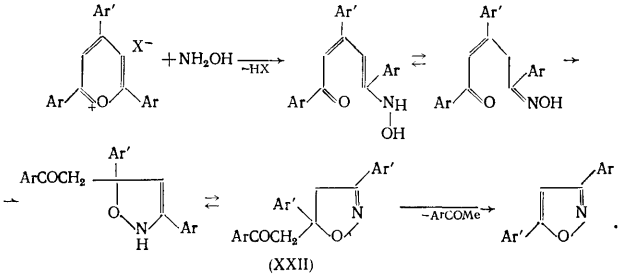


The reaction with cyanoacetamide and cyanoacetanilide in the presence of bases proceeds without the involvement of the cyano-group in the formation of the pyridine ring[58]:



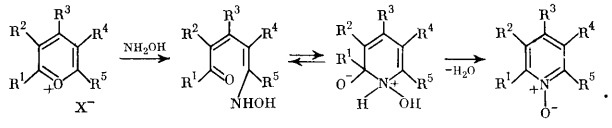
R = H, Ph .

Triarylpyrylium salts react with hydroxylamine in neutral or basic media to form phenacyl derivatives of isoxazolines (XXII), which decompose on heating into acetophenone and 3,5-diphenylisoxazoles[154,155]:



(XXII)

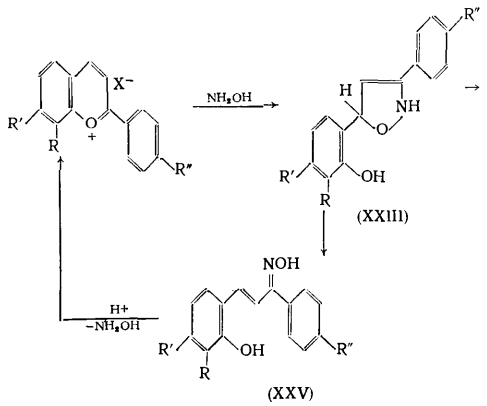
In an acid medium arylpyrylium salts react with hydroxylamine and are converted into the *N*-oxides of arylpyridines[156]:



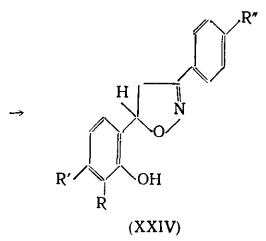
Together with the *N*-oxides, the reactions of 2,4,6-triarylpyrylium salts give rise under these conditions to isoxazolines (XXII) and their oximes. In the presence of even one additional substituent in the 3- or 5-position in the pyrylium ring the reaction proceeds exclusively with formation of pyridine *N*-oxides. The formation of 2,4,6-trimethylpyridine *N*-oxide in the reaction of TMPP with hydroxylamine takes place in both acid and basic media.

The reaction of heteroarylpyrylium salts with hydroxylamine yielded isoxazoles[15,16,157], while isoquinoline *N*-oxide was obtained from 1,3-dimethyl-2-benzopyrylium perchlorate[65].

The reaction of flavylium salts with hydroxylamine leads to *o*-hydroxyphenylisoxazolines (XXIII), which can be made to undergo a thermal rearrangement to isoxazolines (XXIV) or can be converted in acid media into oximes (XXV), which recyclise to the initial flavylium salt by eliminating a hydroxylamine molecule[158]:



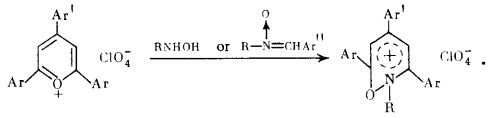
(XXV)



(XXIV)

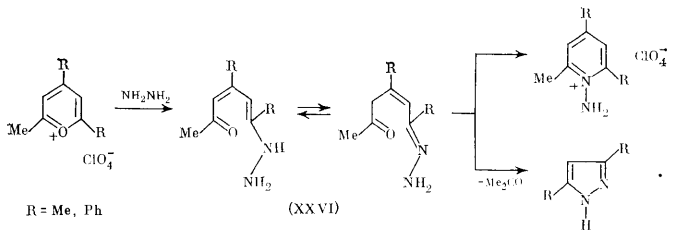
4-Ethoxyflavylium perchlorate reacts with hydroxylamine to form flavone oxime[79].

The reaction of substituted arylhydroxylamines with 2,4,6-triarylpyrylium salts in DMF is accompanied by ring expansion, which leads to the synthesis of a new seven-membered cation with eight π electrons—1,2-oxazepinium[159]:



The same cations have been obtained by the reaction of 2,4,6-triarylpyrylium salts with aldonitrones[159].

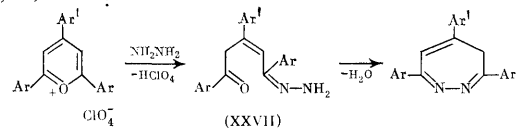
In the presence of a 2-alkyl substituent, pyrylium perchlorates react with hydrazines (1:1 reaction ratio) to form *N*-aminopyridinium salts[160]:



R = Me, Ph (XXVI)

1-Amino-octahydroacridinium[161], 1-amino-2,6-dimethyl-4-(2-benzothiazolyl)pyridinium[16], and 12-amino-11,13-dimethyl[9]-(2,6)pyridinophanium[22] salts have been obtained analogously. The intermediate hydrazone (XXVI) can split off an acetone molecule under mild conditions on treatment with an excess of hydrazine and cyclise to a pyrazole derivative[161].

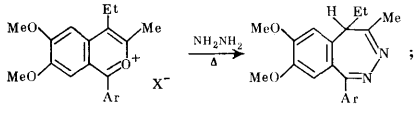
The reaction of arylpyrylium salts with hydrazine is accompanied by ring expansion with formation of 4*H*-1,2-diazepines[57,154,162-164]:



(XXVII)

It has been possible to isolate the intermediate monohydrazone (XXVII), whose intramolecular condensation leads to 1,2-diazepine[165]. 1,2-Diazepines with t-butyl[166] and methyl[58] substituents in the 3- and 7-positions have also been obtained.

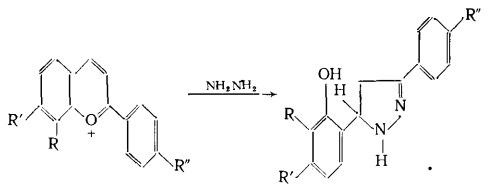
1-Aryl-2-benzopyrylium salts react with hydrazine and are converted into 5*H*-2,3-benzodiazepines[167]:



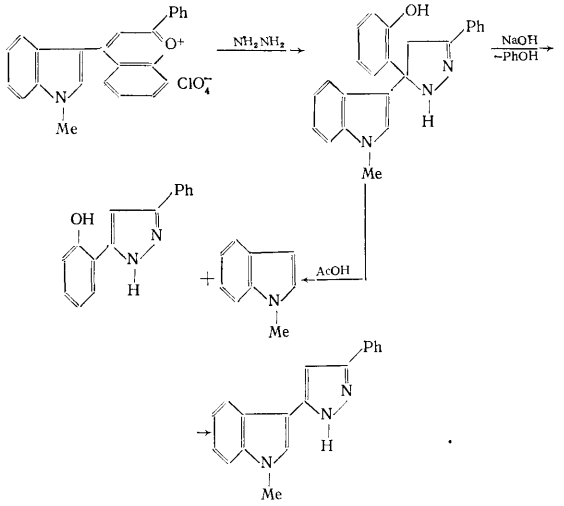
Ar = 3,4-dimethoxyphenyl; X = Cl, Br, HSO_4, ClO_4 .

Flavylium salts with the free 4-position are attacked by hydrazine exclusively in the 2-position. The addition product then isomerises with the opening of the pyran ring and

cyclises to 4,5-dihydro-1*H*-pyrazole[158]:

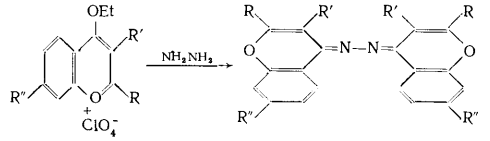


4-Indolylflavylium salts react with hydrazine analogously, but in the presence of a base pyrazoline splits off the phenolic substituent, forming 3-(5-pyrazolo)indole[166]:

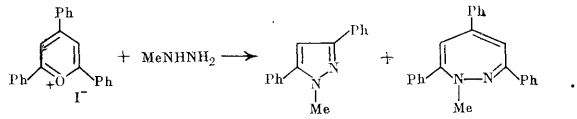


On being refluxed in acetic acid, pyrazoline is cleaved to 1-methylheteroindole and 5-*o*-hydroxyphenyl-3-phenylpyrazole.

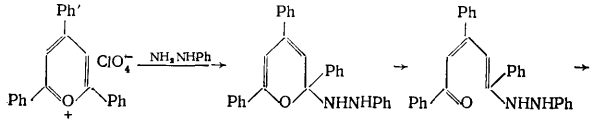
On reaction with hydrazine, 4-ethoxy-1-benzopyrylium salts give rise to chromone azines[79]:

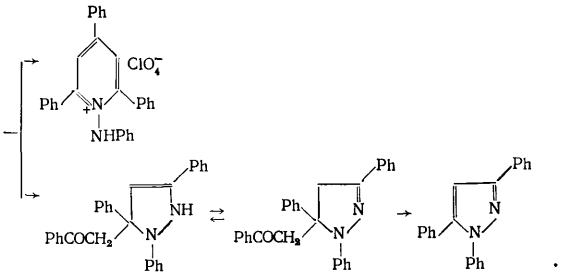


The reaction of 2,4,6-triphenyl- and 2-methyl-4,6-diphenylpyrylium salts with methylhydrazine results in the formation of substituted pyrazoles and a small amount of phenacylmethylpyrazolines, 1-methyl-3,5,7-triphenyl-1*H*-1,2-diazepine having been obtained in 4% yield only from 2,4,6-triphenylpyrylium iodide[168]:

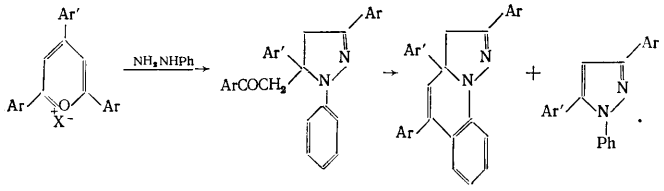


The reaction of 2,4,6-trisubstituted pyrylium salts with an equimolar amount of phenylhydrazine leads to *N*-phenylaminopyridinium salts[169]. On reaction with twice the amount of phenylhydrazine, TPPP recyclises to phenacylpyrazoline, which can split off acetophenone, being converted into pyrazole[154]:





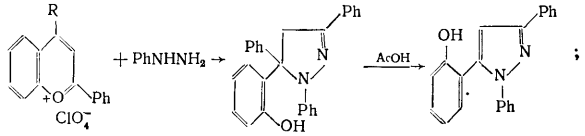
In the presence of a large excess of phenylhydrazine, the resulting phenacylpyrazolines are capable of intramolecular condensation to 4*H*-pyrazolo[2,3-*a*]quinoline[170]:



At the same time the pyrazoline is aromatised to pyrazole, while eliminating acetophenone.

The corresponding pyrazoles have been isolated in the reaction of 4-(2-benzothiazolyl)-2,6-dimethyl-[16] and 4-(1-alkyl-3-indolyl)-2,6-diphenylpyrylium salts[171] with phenylhydrazine.

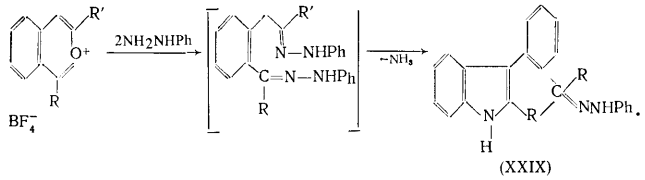
1-Benzopyrylium[166] and pyrylia[2,3-*c*]indole salts[157] react with phenylhydrazine to form pyrazolines, for example (XXVIII):



(XXVIII)

R = 1-methyl-3-indolyl.

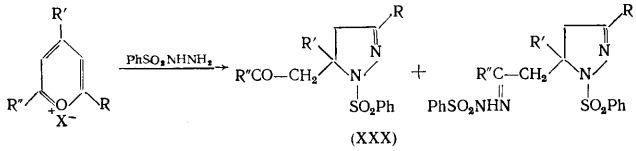
The reaction of 2-benzopyrylium salts with phenylhydrazine gives rise to substituted indoles (XXIX), probably via an intermediate bisphenylhydrazone, as in the Fischer synthesis of indoles[49]:



(XXIX)

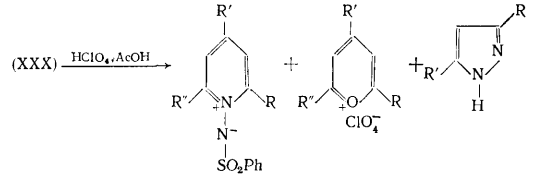
Examples of the conversion of pyrylium salts into 1-phenyl-1*H*-1,2-diazepines are as yet unknown.

Benzenesulphonyl hydrazide reacts with arylpyrylium salts to form pyrazolinylacetophenones (XXX) or a mixture of the latter with their benzenesulphonylhydrazones[172]:



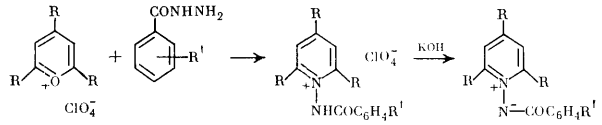
(XXX)

It is of interest that treatment of the pyrazolines (XXX) with $HClO_4$ in acetic acid can effect their recyclisation either to *N*-pyridiniabenzenesulphimide or a pyrylium salt, depending on the nature of the aryl substituent[173]:

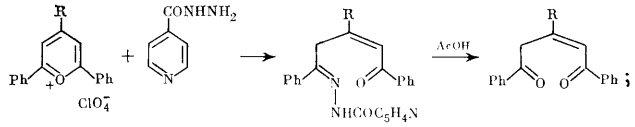


For R′ = R″ = Ph and R = *p*-$NO_2C_6H_4$, a mixture of three products is obtained, for R′ = R″ = Ph and R = *p*-BrC_6H_4, only the pyrylium salt is formed, and for R″ = Me and R = R′ = *p*-$NO_2C_6H_4$, the only product is a betaine.

The reactions of substituted benzoyl hydrazides with pyrylium salts proceed similarly to the reactions with aromatic amines, giving rise to the formation of 1-acylaminopyridinium salts, whose treatment with alkali leads to acyliminopyridinium betaines[161,174,175]:



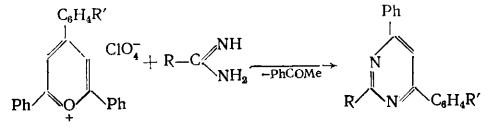
When arylpyrylium perchlorates are refluxed in DMF with twice the amount of benzoyl or isonicotinoyl hydrazide, pentene-1,5-dione monobenzoyl- or monoisonicotinoylhydrazones are formed and are then hydrolysed to the 1,5-diketones on refluxing in acetic acid[171]:



R = 1-benzyl-3-indolyl, 1-methyl-3-indolyl, or phenyl.

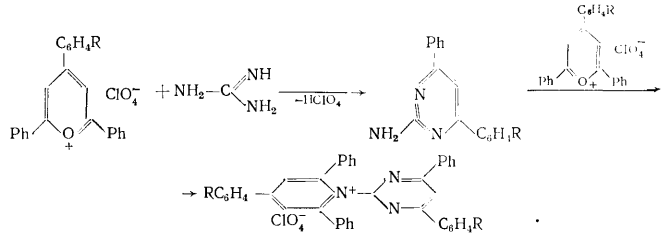
V. REACTIONS WITH POLYFUNCTIONAL AMINES CONTAINING THE N—C—N GROUP

It has been observed recently that the reactions of 2,4,6-triarylpyrylium perchlorates with amidines involve both amino-groups of the latter, which leads to the formation of 2,4,6-triarylpyridines[176,177]:

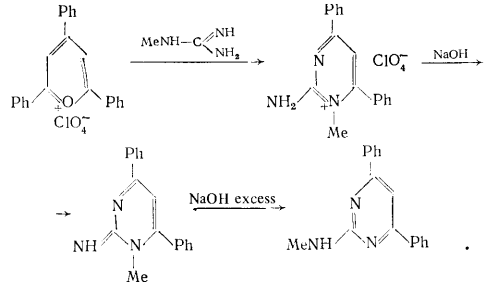


Pyrylium salts unsubstituted in the 4-position interact with amidines similarly, forming 2,4-diarylpyrimidines[177]. Methylpyrylium salts are not converted into pyrimidines on treatment with amidines.

The recyclisation of 2,4,6-triarylpyrylium perchlorates on reaction with guanidine leads to the intermediate 2-aminopyrimidines, which react with the initial pyrylium salt[178,179]:

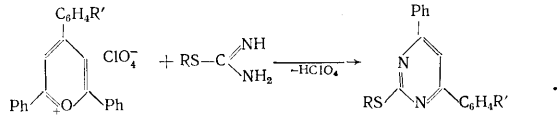


When the same pyrylium salts react with methylguanidine, the pyrylium cation is attacked preferentially by the more basic methylamino-group of the nucleophile. The structure of the resulting unstable 2-iminodihydropyrimidine has been confirmed by the Dimroth rearrangement to 2-methylamino-4,6-diphenylpyrimidine[179]:



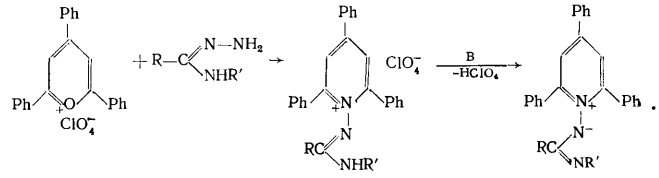
TMPP and TPPP react with sulphanilylguanidine via one amino-group of the guanidine fragment, forming the corresponding pyrimidinium salts[179]. The formation of the pyrimidine ring might have been expected also in the reaction of pyrylium salts with urea or thiourea. However, the interaction of these compounds and of *N*-substituted ureas with TPPP in DMF leads to pyridine (V)[180].

In contrast to ureas and thiourea, S-substituted isothioureas react readily with pyrylium salts, forming 2-alkylthio-4,6-diarylpyrimidines[180,181]:

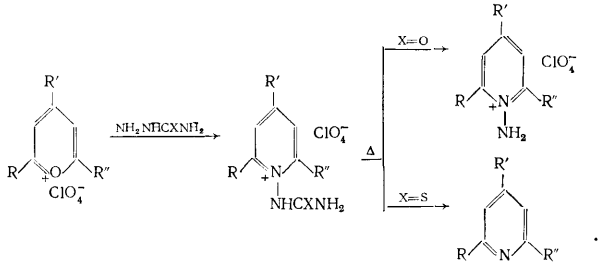


2-Methyl-4,6-diphenylpyrylium perchlorate and TMPP are converted into the corresponding pyridines by reaction with *S*-benzylisothiourea. Evidently, the electrophilicity of the C(4) atom in these salts is insufficient for cyclisation to pyrimidine.

In the reaction with TPPP under mild conditions, amidrazones form 2,4,6-triphenylpyridinium salts, which are readily deprotonated in the presence of bases to substituted pyridinium *N*-ylides[182,183]:

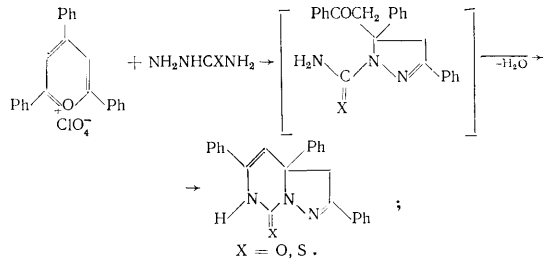


The reactions of 2,4,6-trisubstituted pyrylium salts with semi- and thiosemi-carbazides in ethanol involve one amino-group of the hydrazine fragment and lead to *N*-carbamido- and *N*-thiocarbamido-pyridinium salts[180]:



N-Carbamidopyridinium salts undergo thermal cleavage in DMF, which constitutes a convenient method of preparing *N*-aminopyridinium salts. *N*-Thiocarbamidopyridinium salts undergo thermal degradation in boiling DMF via a different mechanism involving the elimination of the corresponding pyridines[180].

When TPPP is refluxed with semi- and thiosemi-carbazides in DMF, the reaction involves the second amino-group of the hydrazine fragment of the latter and a pyrazoline ring is formed. Subsequent intramolecular condensation of the amino-group with the carbonyl group of the phenacyl substituent completes the formation of a new bicyclic system—7-hydroxy(mercapto)-2,3a,5-triphenyl-3*H*-pyrazolo[1,5-c]-pyrimidine[184]:



Thus the interaction of arylpyrylium and 2-benzopyrylium salts with nitrogen-containing nucleophiles takes place via the attack of the latter on the carbon next to the oxygen atom and subsequent recyclisation if this is possible. In pyrylium salts with functional and alkyl substituents and also in the salts with an unsubstituted electron-deficient position, an additional electrophilic centre appears and the reactions proceed via one pathway or another depending on the reactant and the process conditions.

Under the influence of the condensed benzene ring, 1-benzopyrylium salts lose their ability to exchange the heteroatom.

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The data presented in this review demonstrate the likely usefulness of pyrylium salts as synthons in organic chemistry, since numerous aliphatic, aromatic and heterocyclic functional derivatives as well as pyridines, pyridinium salts, pyrazoles, isoxazoles, pyrimidines, diazepines, 1,3-oxazepines, 1,2-oxazepinium salts, and various condensed heterocyclic compounds can be obtained from them.

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