Translated from *Uspekhi Khimii*, **43**, 1739-1770 (1974) U.D.C. 547.81 : 542.958.4 + 547.512 + 547.834.31

The Reactions of Certain Aromatic Cations

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The review gives a systematic account of the most characteristic reactions of heteroaromatic cations and also tropylium and cyclopropenylium salts. The properties of these cations are compared and classified in accordance with three types: 1. reactions involving recyclisation; 2. reactions of substituents in aromatic cations; 3. reactions with retention of the ring. Attention has been concentrated on the recyclisation reactions and studies which have not been described in previous reviews. The bibliography includes 220 references.

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I. INTRODUCTION

There has been a considerable growth of interest recently in cyclic aromatic cations. Most attention has been devoted to pyrylium salts owing to their unique capacity to be converted into a wide variety of benzenoid, non-benzenoid aromatic, and heterocyclic compounds. Such reactions are not characteristic of thia- and selenapyrylium, flavylium, and xanthylium salts, their reactions proceeding mainly with retention of the initial ring. Tropylium and cyclopropenylium cations—the most typical representatives of charged non-benzenoid aromatic systems—have also attracted much attention. The purely theoretical interest in these compounds has been combined with a search for their direct practical applications, which has led to important results. Thus certain derivatives of pyrylium salts enter into valuable light-sensitive compositions for electronic engineering (see, for example, Refs. 1 and 2). Extensive experimental data on the reactions of aromatic cations have now accumulated. On the other hand, many of the available reviews are devoted mainly to the synthesis of these compounds (see, for example, Refs. 3–10) and no systematic account has been given of the reactions of the cations. Dimroth's review of the reactions of pyrylium salts and aromatic compounds[4] is an exception. Ring expansion reactions of cyclopropenylium cations, ring contraction reactions of tropylium cations, a number of new examples of the recyclisation of pyrylium salts, and also numerous reactions of heteroaromatic cations with retention of the ring were discovered in recent years. Therefore the present review is restricted to a brief consideration of the transformations of pyrylium salts into aromatic systems, attention being concentrated on studies of the reactions of aromatic cations which have not been described in the reviews published previously.

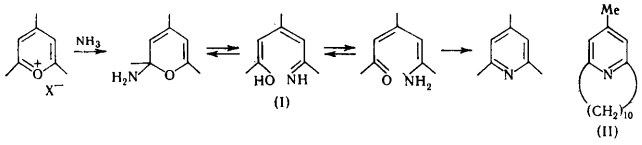
All the reactions of aromatic cations can be divided into three main types: 1. reactions of aromatic cations involving recyclisation; 2. reactions of substituents in aromatic cations; 3. reactions with retention of the ring.

II. REACTIONS OF AROMATIC CATIONS INVOLVING RECYCLISATION

When nucleophilic agents add to aromatic cyclic cations, their aromaticity is destroyed which frequently leads to ring opening. If there is a possibility of the formation of a new aromatic system, the open-chain form cyclises.

1. Pyridines and Pyridinium Salts. *N*-Oxides

The most typical example of the reactions of pyrylium salts is their interaction with ammonia and its derivatives leading to the formation of pyridine and other heterocyclic nitrogen-containing bases. In an early study Baeyer[11] established that pyrylium salts are readily converted into pyridine derivatives on heating with an aqueous ammonium carbonate solution. After Baeyer and Piccard[12], Dilthey[13], Gastaldi[14], and Balaban and Nenitzescu[15] synthesised a series of substituted pyridines from the corresponding pyrylium salts. The reaction almost always proceeds readily and with a quantitative yield. It is convenient to employ aqueous and alcoholic ammonia solutions[11,13] or ammonium acetate in acetic acid[16]. The reaction mechanism consists of nucleophilic attack by ammonia on the α-position of the pyrylium ring, the opening of this ring, and subsequent closure of the pyridine ring[17]:

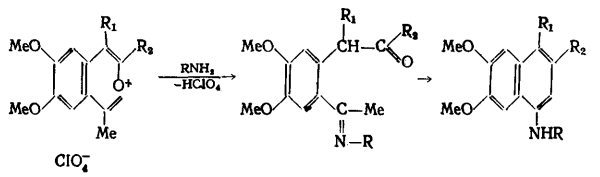


Balaban and Toma succeeded in isolating the intermediate iminoenols[17]. The conversion of the pyrylium salt into a pyridine derivative does not occur when the oxygen atom of the pyrylium salt heteroring is provided by the phenolic component, i.e. neither chromylium nor xanthylium salts can be converted into quinolines or acridines[18,19]. However, Dimroth[19] found that naphthopyrylium salts nevertheless react with ammonia to form benzoquinoline derivatives.

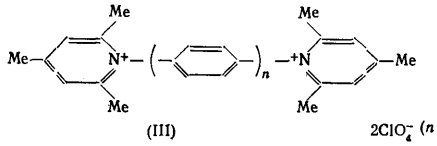
5,6,7,8-Tetrahydrochromylium[20–26] and 2-benzopyrylium[24–26] salts as well as a number of salts condensed with pyrrole, thiophen, indole, and selenophen rings[23,24,26–30] or steroid moieties[31,32] are also capable of being converted into the corresponding pyridine derivatives. Balaban et al. used this reaction to synthesise compound(II)—an analogue of natural muscopyridine[33].

Like ammonia, primary aliphatic and aromatic amines interact with 2,4,6-trisubstituted pyrylium salts, forming *N*-alkyl- and *N*-aryl-pyridinium salts[11,17,34]. A number of investigators[11,12,15,17,34] used this method to prepare pyridinium compounds which are otherwise difficult to obtain.

A non-trivial reaction of primary amines with 2-benzopyrylium salts, leading to naphthylamines, has been described[35]:

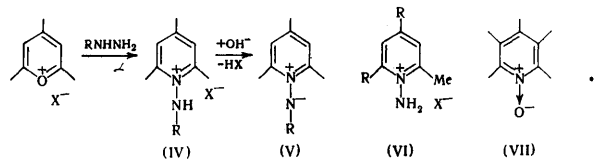


2,4,6-Trimethylpyrylium perchlorate reacts with aromatic diamines to form bispyridinium salts (III):[36]



(III) $2ClO_4^-$ ($n = 1, 2$)

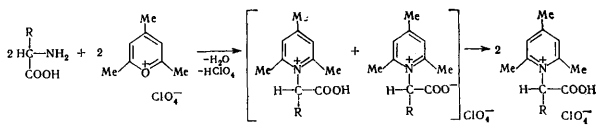
Phenylhydrazine, α-methylphenylhydrazine[4,37,38], and semicarbazide[15] behave similarly, the products being aminopyridinium salts of type (IV). In the presence of bases the salts (IV) are converted into coloured pyridine-betaines (V):[39,40]



(IV) (V) (VI) (VII)

Hydrazine hydrate leads to 1-aminopyridinium salts (VI).[41] A similar reaction has been described for *sym*-octahydroxanthylium[42]. Pyrylium salts react with hydroxylamine form the *N*-oxides of substituted pyridines (VII).[15,43] *p*-Hydroxyphenylpyridinium salts (obtained from pyrylium salts and aminophenols), which are converted by bases into pyridinia-*N*-phenol-betaines[44,45], are interesting.

Certain aminoacids, aminoacid esters, and peptides react with pyrylium salts via the amino-group to form quaternary pyridinium derivatives of aminoacids, peptides, and pyrimidines[34,46-48]. It is suggested that the interaction of aminoacids and peptides with 2,4,6-trimethylpyrylium proceeds via the formation of the betaines (VIII), which are then converted into the pyridinium salts (IX):

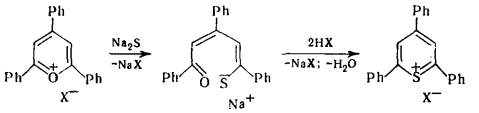


(VIII) (IX)

It has also been suggested that pyrylium salts can block the primary amino-groups in biological systems without involving other functional groups. This can occur in reactions with aminoacids and proteins but not with aminopurines, aminopyrimidines, nucleotides, and nucleic acids[47,48].

2. Thiapyrylium Cations

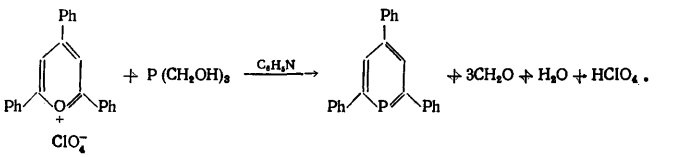
The addition of sodium sulphide to pyrylium salts leads to the opening of the pyran ring. After the addition of an inorganic acid, the resulting open-chain species undergoes ring closure at the sulphur atom. The reaction usually proceeds in acetone, the products being thiapyrylium salts[49]. Wizinger and Ulrich[49,50] proposed the following reaction mechanism:



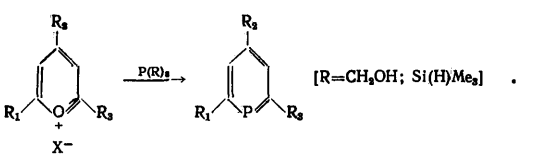
The reaction of chromylium and isochromylium salts with sodium sulphide in aqueous acetone solution does not result in the formation of the corresponding benzothiapyrylium salts[19].

3. Phosphabenzene Derivatives

The attempts to synthesise phosphorin—a representative of a new class of heterocyclic compounds—were undertaken a long time ago[51]. Success was achieved for the first time by Märkl[52], who obtained 2,4,6-triphenylphosphabenzene from 2,4,6-triphenylpyrylium perchlorate and tri(hydroxymethyl)phosphine by the reaction



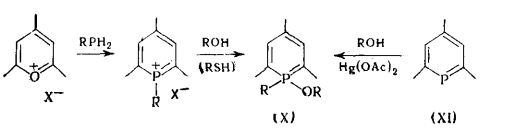
Subsequently Tolmachev and Kozlov extended this method to various pyrylium salts[53] and Zhungietu et al.[54] extended it to indolyl- and pyrrolyl-pyrylium salts[54]. Three main methods for the synthesis of phosphabenzene derivatives from pyrylium salts are now known: 1. from tri(hydroxymethyl)phosphine in pyridine[52]; 2. from tris-(trimethylsilyl)phosphine in acetonitrile[55]; 3. from phosphine in butyl alcohol under pressure[56]:



We may note that the third method is the most general and is suitable for the synthesis of any alkyl- or aryl-phosphabenzene.

Benzophosphorins cannot be obtained from chromylium salts. Nor is oxygen replaced by phosphorus in isochromylium salts[55,57]. The recyclisation (carried out by Dimroth[19]) of naphthopyrylium salts into naphthophosphorins is therefore particularly interesting.

The syntheses of the various *P*-substituted phosphorins (X) (1-aryl-, 1-alkyl-, 1-alkoxy-, or 1-mercapto-phosphabenzene) are possible[58,59] both directly from pyrylium salts and primary phosphines and via compounds (XI) by the reaction



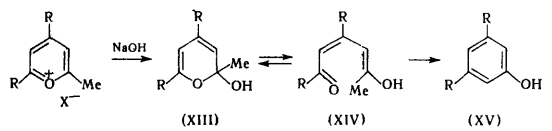
(X) (XI)

Dimroth described the conversion of 2,4,6-triphenylphosphabenzene into the corresponding anion[57], radical, radical-anion[57], and dianion, and also its oxidation to the

radical-cation[60]. Phosphabenzenes constitute a unique heterocyclic system the formation of which involves the *d*-orbitals of phosphorus. A number of studies have been made on the physical and chemical properties of phosphorins[55-62].

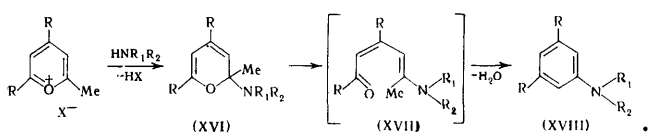
4. Aromatic Hydrocarbons and Their Functional Derivatives

Trisubstituted pyrylium salts containing an α-methyl group in the ring are converted into substituted phenols on refluxing with a 10% solution of alkali[11,14,15]. This reaction, which has been discovered by Baeyer and Piccard[12], proceeds via the intermediate formation of the pseudobase (XIII), which is converted into compound (XV) via the tautomeric ketone (XIV):



(XIII) (XIV) (XV)

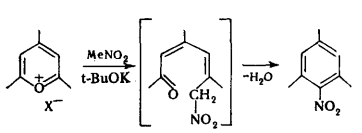
Deuterated alkylphenols have been obtained in this way[63]. Dulenko and coworkers used this reaction to synthesise thionaphthene and selenonaphthene systems[64]. The addition product (XVI) undergoes ring opening when acted upon by both secondary amines and alkali. The intermediate (XVII) subsequently condenses to *NN*-disubstituted amines (XVIII)[65]:



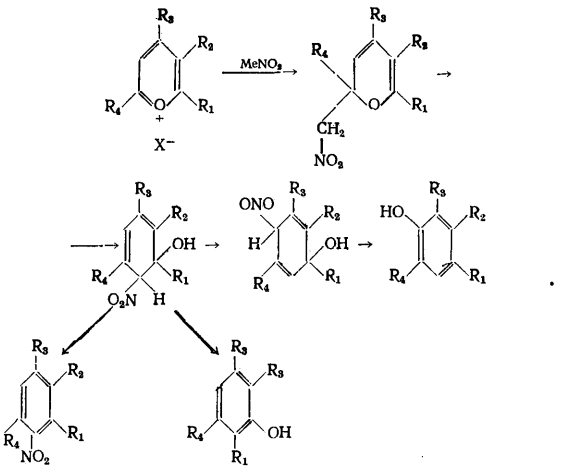
(XVI) (XVII) (XVIII)

The reaction is of interest for the synthesis of certain tertiary aromatic amines which are otherwise difficult to obtain, for example aminostilbenes[66]. *N*-Arylindolines have been obtained in this way from indoline[67].

Dimroth and coworkers[68-70] discovered a novel method for the preparation of alkyl- and aryl-substituted nitrobenzenes by the reaction of pyrylium salts with nitromethane in the presence of potassium t-butoxide. The reaction proceeds as follows:

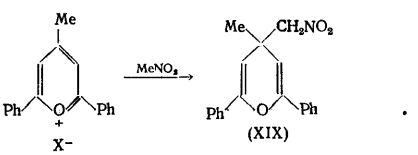


Phenylenebispyrylium salts yield the corresponding terphenyls[71]. When this reaction is carried out in the presence of one mole of base (potassium t-butoxide) in chlorobenzene, dichloroethane or ethyl alcohol, substituted phenols are obtained[72]:



Chromylium salts do not react with nitromethane and isochromylium salts are also not converted into 2-nitronaphthalene derivatives (according to Dimroth's data[70]). 2,4-Diphenyl-5,6,7,8-tetrahydrochromylium fluoroborate can be successfully converted into the corresponding 1-nitro-2,4-diphenyltetrahydronaphthalene[4].

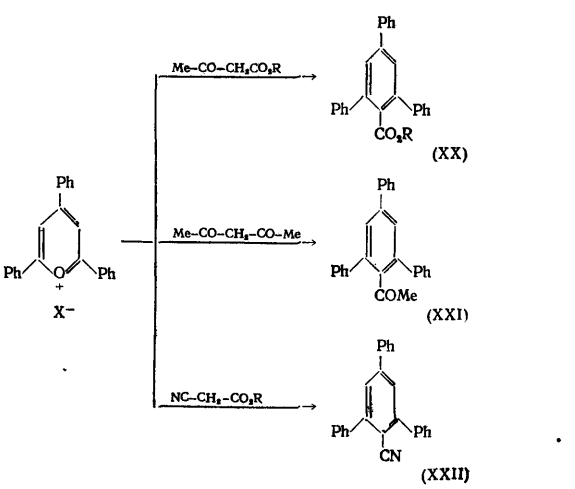
If the 4-position is free or contains the methyl group, the addition of CH_3NO_2 with formation of the stable pyran (XIX) is sterically more favourable[4]:



(XIX)

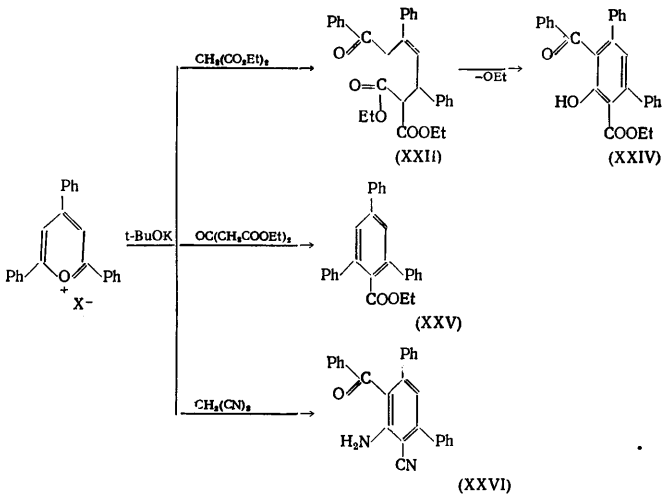
Trisubstituted pyrylium salts react with phenylnitromethane to form tetrasubstituted nitrobenzenes[73].

Compounds containing an active methylene group also react to form benzene derivatives. Their reaction with 2,4,6-triphenylpyrylium in the presence of two moles of potassium t-butoxide leads to the elimination of the acetyl or ethoxycarbonyl group with subsequent formation of the benzene derivatives (XX), (XXI), and (XXII)[74]:



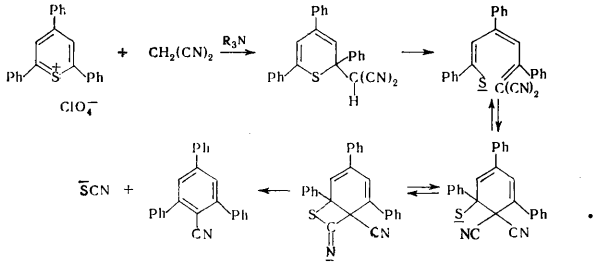
(XX) (XXI) (XXII)

The interaction of triarylpyrylium cations with malonic ester leads to the ring-opening product (XXIII), which recyclises without the elimination of the ethoxycarbonyl group to the benzene derivative (XXIV). The reaction with the diester of acetonedicarboxylic acid leads similarly to the formation of the benzoate ester (XXV) and the reaction with malonodinitrile results in the formation of the aminonitrile (XXVI) [75]:

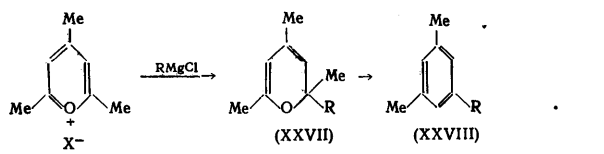


(XXII) (XXIV) (XXV) (XXVI)

In the series of heteroaromatic cations reactions involving recyclisation to benzene derivatives are characteristic only of pyrylium salts. The single instance of the conversion of 2,4,6-triarylthiapyrylium into a substituted benzonitrile has been described [76]. This reaction is believed to proceed via the mechanism:

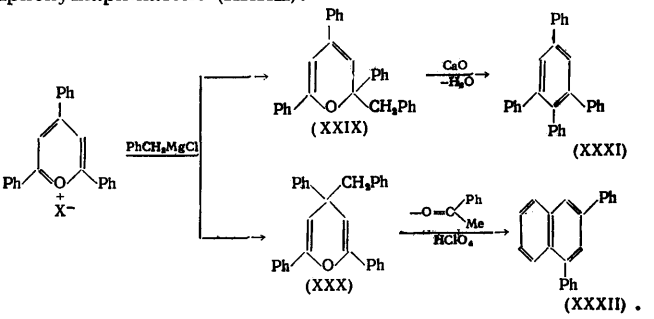


When 2,4,6-trisubstituted pyrylium salts are acted upon by a Grignard reagent, the nucleophilic addition of the organomagnesium compound takes place preferentially in the α-position of the pyran ring. If this position of the pyran (XXVII) contains a methyl or methylene group, recyclisation to the substituted benzene (XXVIII) takes place [71,73]:



(XXVII) (XXVIII)

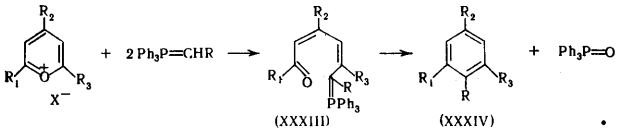
Benzyl-lithium or benzylmagnesium chloride acts similarly on 2,4,6-triphenylpyrylium. On heating with CaO, the product (XXIX) is converted into tetraphenylbenzene (XXXI), while the product (XXX) gives rise to diphenylnaphthalene (XXXII): [68,75,77]



(XXIX) (XXXI) (XXX) (XXXII)

Phenanthrene and benzothiophen derivatives were obtained in the same way [75,77].

Thus there are two methods for the recyclisation of pyrylium salts into benzene derivatives: (1) by using the α-methyl group of the pyrylium ring and (2) by the introduction into the ring of a carbon atom of the nucleophilic component. Preference must be given to the second method, since it is more universal and leads to a wide range of aromatic compounds. A novel instance of the conversion of triarylpyrylium salts into benzene derivatives by an intramolecular Wittig reaction has been described by Märkl [78]:

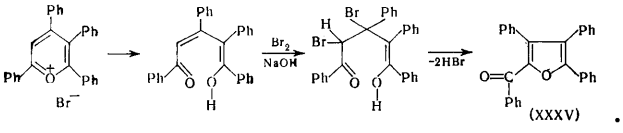


(XXXIII) (XXXIV)

The intermediate phosphoranes (XXXIII) can be isolated or converted immediately into hydrocarbons of type (XXXIV).

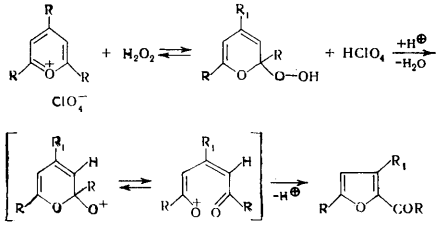
5. Ring Contraction Reactions

An important feature of certain aromatic cations is their ability to undergo ring contraction reactions under the influence of inorganic nucleophiles. This is most typical for pyrylium salts. Thus in an early investigation Dilthey [79,80] found that 2,3,4,6-tetraphenylpyrylium bromide is converted into the furan (XXXV) by the reaction

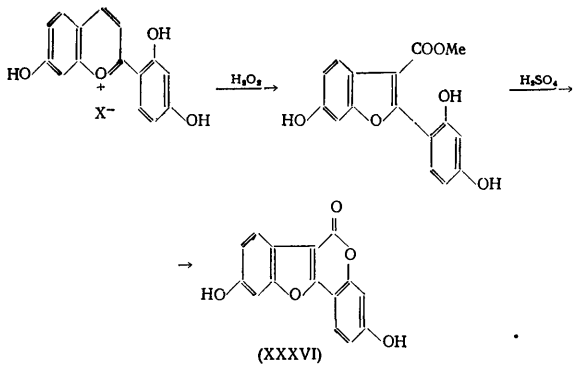


(XXXV)

Balaban and Nenitzescu [63,81] achieved the recyclisation of trialkylpyrylium salts into furans with the aid of hydrogen peroxide and proposed the following reaction mechanism:

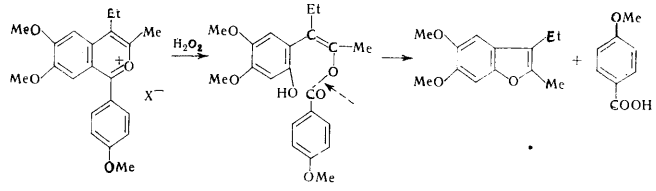


Benzopyrylium salts react with hydrogen peroxide to form benzofuran derivatives. Coumoestrol (XXXVI), an oestrogenic plant preparation, was synthesised in this way [82]:

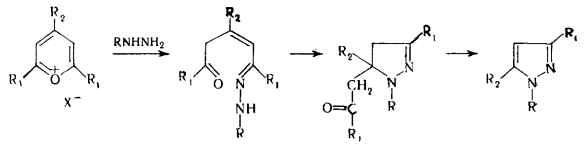


(XXXVI)

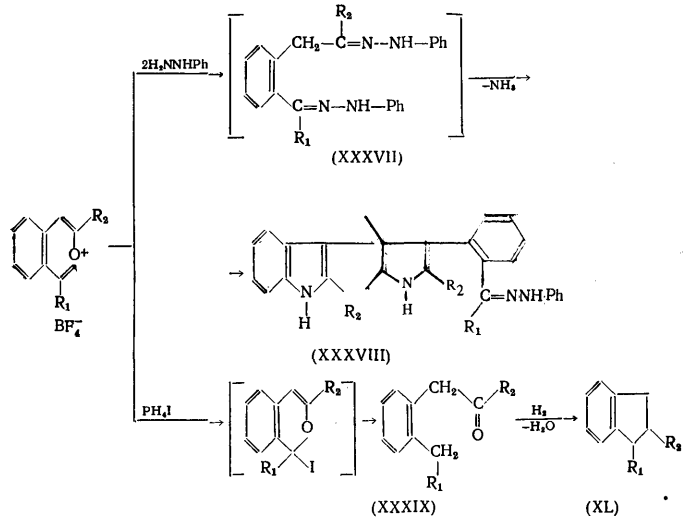
Benzofuran derivatives are also formed when 2-benzopyrylium salts are oxidised by hydrogen peroxide [83]:



When 2,4,6-trisubstituted pyrylium salts are acted upon by two-centre nucleophiles, the reaction probably involves the α- and γ-positions of the pyran ring, which ultimately leads to recyclisation with formation of a five-membered ring containing two heteroatoms. Thus, on reaction with a twofold excess of hydrazine or phenylhydrazine, pyrylium salts are converted into pyrazoles [42,46,84]:

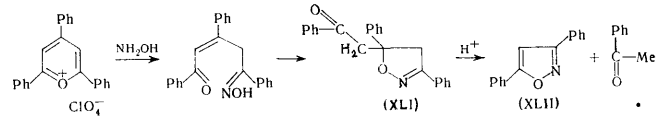


The reaction of chromylium salts with hydrazine and phenylhydrazine also proceeds with ring contraction [85]. When an isochromylium salt reacts with phenylhydrazine, the product is an indole (XXXVIII) formed via the bisphenylhydrazone (XXXVII). [19] The reaction of an isochromylium salt with phosphonium iodide (PH_4I) in glacial acetic acid results in the formation of an indan (XL) via the intermediate ketone (XXXIX) [19] in accordance with the following scheme:



(XXXVII) (XXXVIII) (XXXIX) (XL)

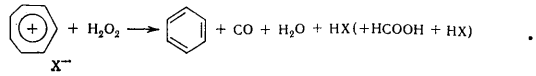
Like hydrazine and phenylhydrazine, hydroxylamine (another two-centre nucleophile) leads to isoxazolines (XLI), which can be readily converted further into isoxazoles (XLII): [84,86]



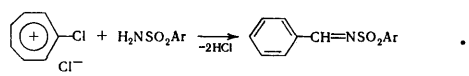
(XLI) (XLII)

Zhungietu and coworkers [87,88] applied this reaction to 4-indolylpyrylium salts and obtained indole derivatives containing isoxazole and isoxazolium rings.

The seven-membered ring of the tropylium cation has been found to contract to a six-membered ring on treatment with hydrogen peroxide. Vol'pin and coworkers [7] showed that, when the tropylium ion is treated with dilute hydrogen peroxide, the products are benzene, carbon monoxide, and formic acid:



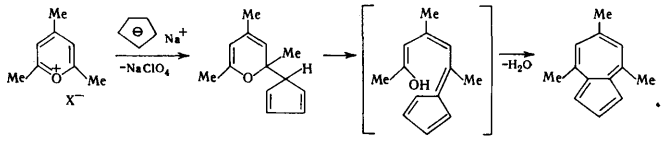
When a chlorine-substituted tropylium cation reacts with sulphonamides in the presence of dimethylamine, a rearrangement with ring contraction also takes place [89]:



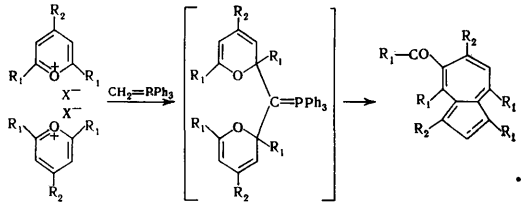
6. The Expansion of the Rings of Aromatic Cations

Formally the reaction of pyrylium salts involving the expansion of the six-membered ring to a seven-membered ring can be represented as the interaction of both α-positions of the pyran ring with a two-centre nucleophilic agent (organic or inorganic). Historically the first

instance of such a reaction was the synthesis of 4,6,8-trimethylazulene by the interaction of 2,4,6-trimethylpyrylium perchlorate with cyclopentadienylsodium in tetrahydrofuran (THF), developed by Hafner and Kaiser [90]:



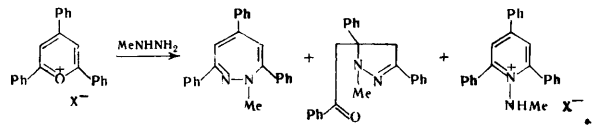
This type of synthesis was extended to other pyrylium salts [91]. When 1,3-dimethyl-5,6,7,8-tetrahydro-2-benzopyrylium perchlorate was allowed to react with cyclopentadienylsodium, 4,10-dimethyl-5,6,7,8-tetrahydrobenzazulene was obtained [92]. The synthesis of azulenes from pyrylium salts by the Wittig reaction proceeds in a somewhat different way [78,93]. Thus methylenetriphenylphosphorane reacts with two molecules of a pyrylium salt as follows:



(XLIII)

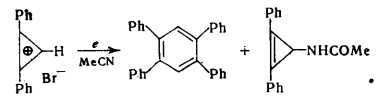
The reaction probably takes place via the intermediate (XLIII).

Pyrylium salts react with alkylhydrazines and hydrazines to form 1,2-diazepines, albeit in low yields [94], the main product being *N*-aminopyridinium salts:

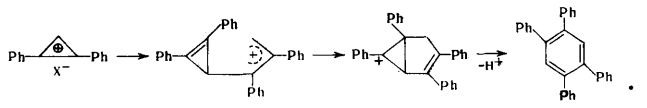


1-Aminopyridinium derivatives, formed from alkylpyrylium salts and hydrazine, can be converted subsequently into diazepines [95]. Zhungietu [88,96] obtained diazepines from indolylpyrylium salts. When 2,4,6-triphenylthiapyrylium tetrafluoroborate was treated with hydrazine, 3,5,7-triphenyl-4*H*-1,2-diazepine was isolated [94]; Balaban confirmed its structure [84,97].

The addition of nucleophilic agents to the cyclopropenylium cation frequently leads to ring opening and the formation of less strained four-, five-, or six-membered cyclic systems. Thus 1,2,4,5-tetraphenylbenzene was isolated on reduction of the 1,2-diphenylcyclopropenylium cation in acetonitrile [98,99]:

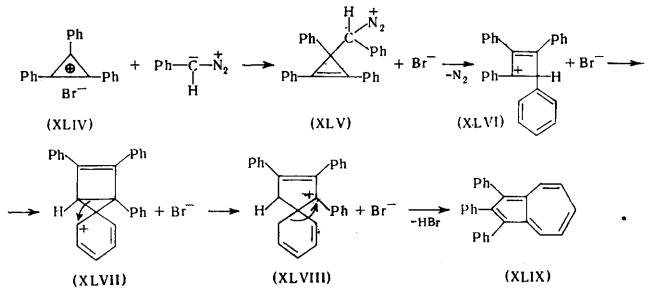


The following mechanism has been proposed on the basis of the structure of the final product for the reaction of the 1,2-diphenylcyclopropenylium cation with cyclopropene leading to tetraphenylbenzene [98]:



The analogous reaction of triphenylcyclopropenylium bromide with 1,2,3-triphenylcyclopropene leads to hexaphenylbenzene. Its yield is small, the main product being 2,3-diphenylindan.

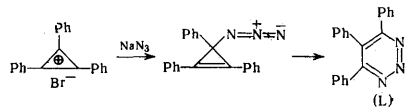
Yet another method for the synthesis, from cyclopropenylium salts, of azulenes which are otherwise difficult to obtain is based on the scheme



(XLIV) (XLV) (XLVI)

(XLVII) (XLVIII) (XLIX)

The addition of phenyldiazomethane to the cation (XLIV) results in the formation of the diazonium salt (XLV), which reacts further in a series of consecutive steps [(XLVI) → (XLVII) → (XLVIII) → (XLIX)]. [99] On reaction with sodium azide, compound (XLIV) is converted into 4,5,6-triphenyltriazine (L): [100,101]

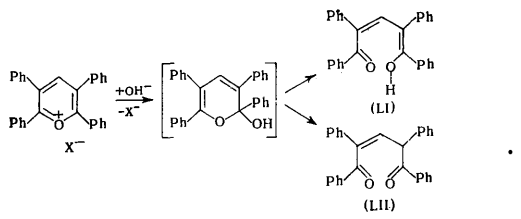


(L)

This reaction, involving the formation of a stable unstrained ring, is typical for many cyclopropene derivatives.

7. Ring Opening

The opening of the rings of cyclic cations whose recyclisation to a new aromatic system is impossible may be regarded as the simplest reaction of aromatic cations with nucleophilic agents. The products of the addition of hydroxide ions [102,103], cyanide ions [104], and phenylhydrazines [105] have been investigated in fair detail. The hydrolysis of 2,3,5,6-tetraphenylpyrylium salts yields two isomers—the enolketone (LI) and a *cis*-diketone (LII):

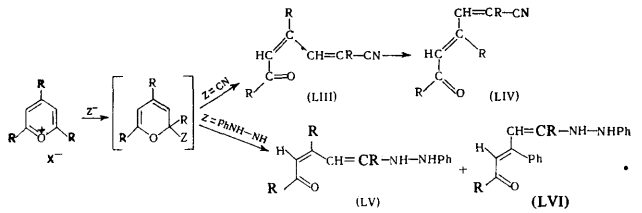


(LI)

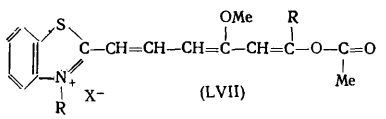
(LII)

Balaban and Nenitzescu [104] established that the cyanide ion reacts with a pyrylium salt to form a cyano-*cis*-alkadienone (LIII), which is converted in an acid medium

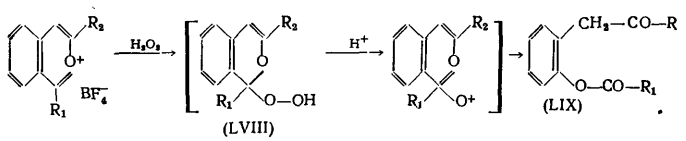
into the *trans*-isomer (LIV). The reaction of arylpyrylium salts with phenylhydrazine gives rise to two isomers and only α-phenylhydrazides (LV) are converted into pyridinium salts[37], while β-phenylhydrazides (LVI) remain in the open-chain form[105]:



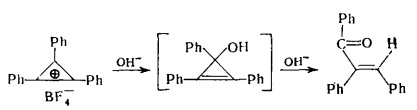
Tolmachev[106,107] studied the interaction of alkoxypyrylium and benzopyrylium salts with quaternary salts of nitrogen-containing heterocycles containing active methyl or methylene groups. The products are cyanines: in certain cases the pyrylium ring is opened and cyanine dyes of type (LVII) are formed:



When isochromylium salts are acted upon by hydrogen peroxide, the oxidation product (LVIII) is formed and then the phenyl ester (LIX). The phenyl ester was also obtained previously by Dilthey[108] from a chromylium salt on treatment with hydrogen peroxide:



Triphenylcyclopropenylium salts readily undergo ring opening merely on treatment with aqueous alkali[109,110]:



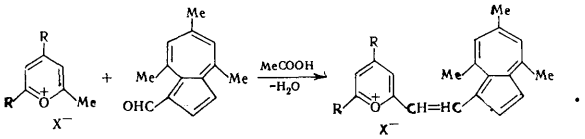
III. REACTIONS OF THE SUBSTITUENTS IN AROMATIC CATIONS

The substituents in aromatic cations alter significantly the course of certain reactions involving the retention of the pyrylium ring. Thus, when pyrylium salts containing methyl substituents are dissolved in heavy water or in deuterated acetic acid, the hydrogen atoms of the methyl groups are replaced by deuterium[63,111,112]. Deuterated or partly deuterated 2,4,6-trimethylpyrylium salts serve as the starting materials for the synthesis of aromatic or heterocyclic compounds with deuterated side chains[113].

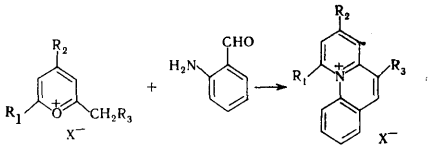
The nitration of 2,4,6-triphenylpyrylium perchlorate involves all three benzene rings, the α-phenyl groups being nitrated in the *meta*-position and the γ-phenyl group in the *para*-position[114-116]. Less active electrophilic agents (acyl and alkyl cations) do not react with phenylpyrylium salts.

1. Condensation via the α- or γ-Methyl Group

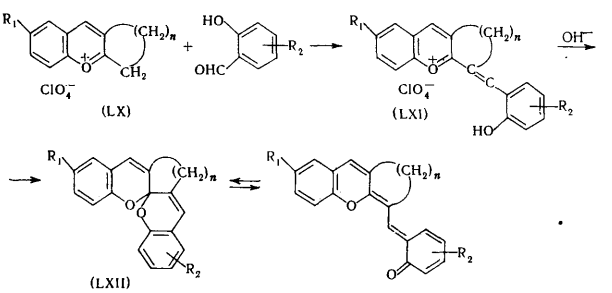
The condensation of α- or γ-methylpyrylium salts with aromatic aldehydes has been examined[117-126]. On reaction with azulenealdehydes, α-methylpyrylium salts give rise to pyrylium derivatives of azulene[127]:



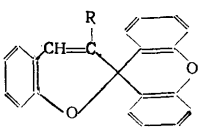
On the basis of the ability of methylpyrylium salts to react with aldehyde and amino-groups, Dimroth[128] proposed a simple method for the synthesis of benzo[*c*]-quinolizinium salts from 2,4,6-trisubstituted pyrylium salts with an α-CH_2R group and 2-aminobenzaldehyde:



The condensation of 3-formylflavene with the methyl groups of various pyrylium salts has been studied[129]. When 1-methyl-3-phenyl-5,6,7,8-tetrahydro-2-benzopyrylium perchlorate was condensed with aliphatic, aromatic, and heterocyclic aldehydes, 1-styryl derivatives were obtained[130,131]. Styryl derivatives of type (LXI), which on treatment with bases are converted into the spiropyrans (LXII), were synthesised from 2,3-cycloalkenobenzopyrylium salts (LX) and *o*-hydroxybenzaldehydes[132]:

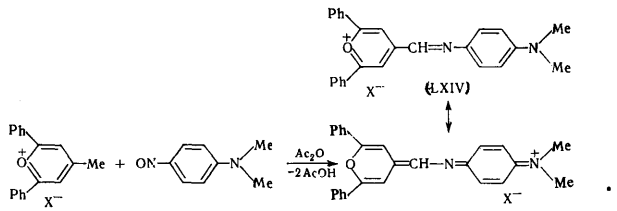


The conversion of styryl derivatives into spiropyrans is possible only for benzopyrylium salts. In the styryl derivatives obtained on the basis of pyrylium salts, the pyrylium ring is opened[132]. The alkyl group in the 9-position of xanthylium salts also condenses with the carbonyl group of aromatic aldehydes[133], forming intensely coloured styrylxanthylium salts[134]:

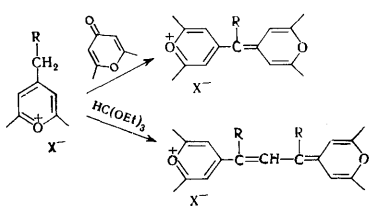


The products of the condensation of alkylxanthylium salts with *o*-hydroxybenzaldehydes are converted into spiropyrans of type (LXIII)[135]. Methyl-, ethyl-, and benzyltropylium salts react similarly with aromatic aldehydes[136], forming styryltropylium salts. Although *NN*-dimethyl-*p*-nitrosoaniline is much less reactive, nevertheless it condenses under severe conditions with α- and γ-methyl or methylene groups to form mesomeric *NN*-dimethylaminophenyliminomethylpyrylium perchlorates [Schiff

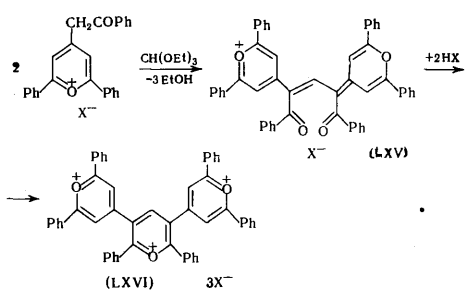
bases of type (XLIV)]. Acid hydrolysis of the resulting ketoimines leads to the corresponding ketones, while aldimines remain unchanged[137]. The following condensation mechanism has been proposed:



The condensation with pyrones takes place under analogous conditions. A number of investigations[138-141] led to the development of a method for the synthesis for pyrylocyanines which are important in practice. Pyrylocyanines are obtained also by the condensation of methyl or methylene derivatives of pyrylium salts with orthoformic ester[142]:

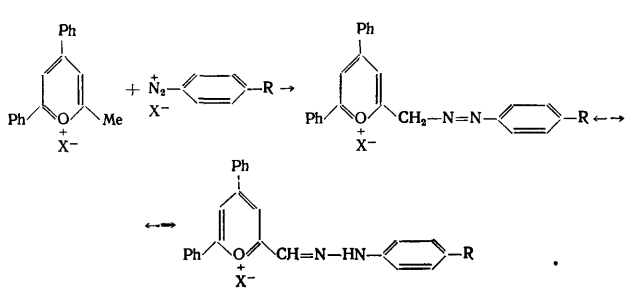


The pyrylocyanine (LXV), obtained from 2,6-diphenyl-4-phenylacylpyrylium and orthoformic ester, cyclises on protonation to the trispyrylium cation (LXVI):[143]



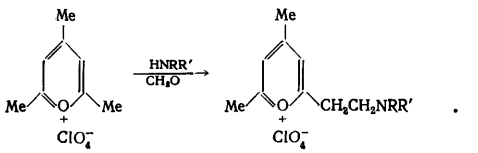
The interaction of pyrones of various pyrylium salts in acetic anhydride has been investigated[139-144]. The products are coloured symmetrical and asymmetric pyrylocyanines.

It was shown[145,146] that, in the presence of hydrogen chloride, 6-methyl-2,4-diphenylpyrylium chloride undergoes azo-coupling with diazonium salts in alcoholic solution:



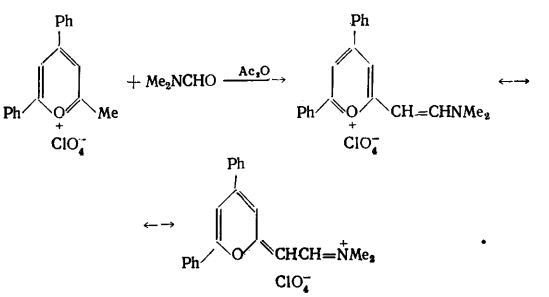
The methyl group in the 9-position of xanthylium also condenses with diazonium salts, forming azo-compounds[147].

Owing to the high reactivity of the hydrogen atoms of the α-methyl groups, it was possible to introduce pyrylium salts into the Mannich reaction with formaldehyde and various amines to form aminopyrylium salts[148]:

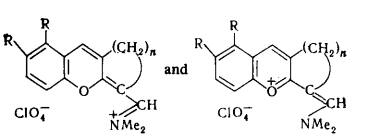


The Mannich reaction has been carried out also with certain natural amines[148].

The reaction of α-methylpyrylium salts with *NN*-dimethylformamide in acetic anhydride yields monoiminium salts, while the reaction with the Vilsmeier complex gives rise to di-iminium salts[149]:



Monoiminium salts can be obtained from alkylpyrylium salts and *NN*-dimethylthioacetamide in acetic anhydride or on the basis of other *NN*-dialkylamides in the presence of phosphoryl chloride. On hydrolysis, the iminium salts give rise to aldehydes or ketones[149]. 2,3-Cycloalkenobenzopyrylium has been formulated and vinylformylated[150]. The compounds obtained can be represented by two formulae:

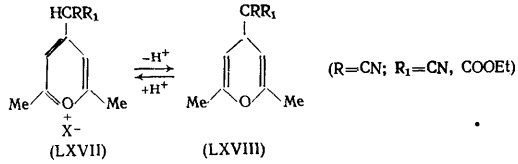


2. Nucleophilic Substitution of the Alkoxy-Groups of Cyclic Cations

The alkoxy-groups in the 4-position of pyrylium salts very readily undergo nucleophilic substitution even by weak nucleophilic agents. Thus, when 4-methoxy-2,6-dimethylpyrylium perchlorate is recrystallised from ethanol, the methoxy-group is substituted by the ethoxy-group, while recrystallisation of the ethoxypyrylium salt from methanol reconverts it into 4-methoxy-2,6-dimethylpyrylium[151]. In water alkoxy-groups are substituted by hydroxy-groups, alkoxypyrylium salts being hydrolysed to pyrones[11]. Thiols (such as phenylmethanethiol) and secondary amines (such as piperidine or morpholine) behave similarly[151,152].

On reaction with 4-alkoxypyrylium salts, sulphides (H_2S, NaHS, and Na_2S) replace alkoxy-groups by mercapto-groups[153]. Compounds containing active methylene groups

displace the methoxy-groups in the pyrylium salts with formation of compounds of type (LXVII), which can be converted into the methylenepyran derivatives (LXVIII)[154]:

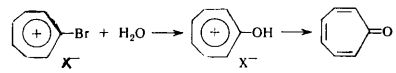


(LXVII) (LXVIII)

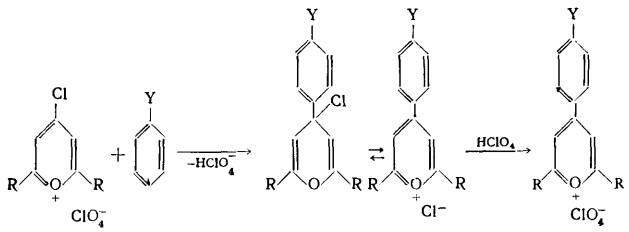
The reaction of methoxytropylium salts with secondary amines in acetonitrile give rise similarly to dialkylaminotropylium derivatives[155]. The reactions of alkoxytropylium and cyclopropenylium cations with various nucleophilic agents have been described[156].

3. Reactions of Halogenopyrylium and Halogenotropylium Salts

The reaction of bromotropylium salts with water results in the formation of tropones[157]:

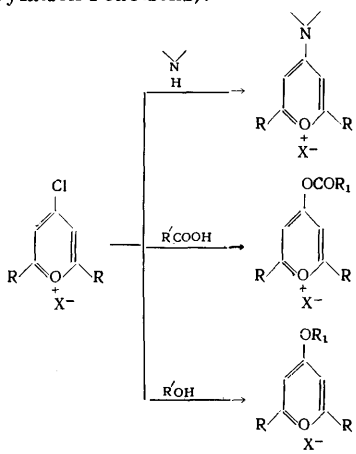


It was shown recently[158,159] that halogenopyrylium salts can react with organic nucleophilic agents to form pyrylium salts with substituents corresponding to the nucleophilic agent employed [salts of type LXIX]:



(LXIX)

The above reaction was also applied to thiapyrylium, benzopyrylium, and xanthylium salts[159]. 4-Halogenopyrylium salts react with secondary cyclic and acyclic amines[160] and also with hydroxy-compounds (alcohols, acids, and phenols)[161] to form amino-, alkoxy-, acyloxy-, and phenoxy-pyrylium salt derivatives respectively (the *N*- and *O*-pyrylation reactions):



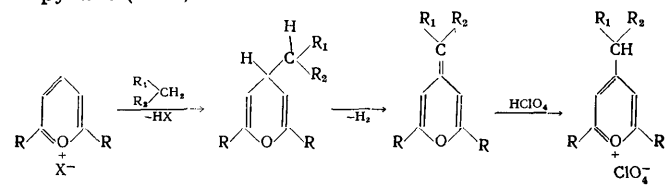
In the reaction of the chlorotropylium cation with alcohols, mercaptans, and alkylarylamines nucleophilic substitution analogous to *N*- and *O*-pyrylation takes place[89,162].

IV. REACTIONS WITH RETENTION OF THE RING

Numerous reactions of aromatic cations with nucleophilic agents take place preferentially with retention of the ring. Monocyclic 2,4,6-trisubstituted pyrylium salts constitute an exception. However, if the γ-position in the pyrylium ring is not substituted, there is a possibility of nucleophilic attack on this free position with formation of the relatively stable 4*H*-pyran.

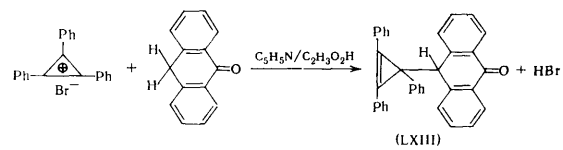
1. Interaction with Compounds Containing Active Methylene Groups and with Organometallic Compounds

2,6-Disubstituted pyrylium cations react with compounds containing active methylene groups in the presence of potassium t-butoxide to form the corresponding 4*H*-pyrans (LXX):[163,164]



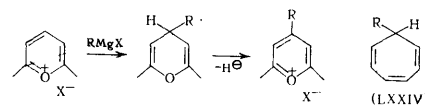
(LXX) (LXXI) (LXXII)

The pyrans (LXX) react with acids to reform the initial salts and only by mild oxidation to (LXXI) or by reaction with triphenylphenoxy-radicals and subsequent treatment with perchloric acid is it possible to convert the system into a new pyrylium salt (LXXII). Wizinger and coworkers condensed pyrylium and thiapyrylium salts with compounds containing active methylene groups in the presence of sodium acetate[165,166]. Similar reactions are also known in the flavylium series[164,167]. Tropylium salts form substituted tropilidenes in reactions of this kind[168,169]. The reactions of tropylium salts with aliphatic aldehydes[170,171], aliphatic and aliphatic-aromatic ketones[169], and compounds containing activated double bonds proceed similarly. In the series of cyclopropenylium cations these reactions have been little investigated. Triphenylcyclopropenylium bromide is known to react with anthrone in the presence of pyridine and acetic acid to form compound (LXXIII):[172]



(LXIII)

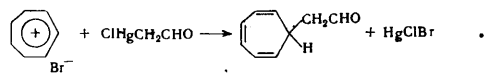
Aromatic cations readily react with organometallic compounds. In an ethereal solution of a Grignard reagent, pyrylium salts are converted into 4*H*-pyrans, which can split off a hydride ion with formation of 2,4,6-trisubstituted pyrylium salts[163]. Thus 2,6-diphenylpyrylium perchlorate can be converted into 4-alkyl-2,6-diphenyl- or 4-aryl-2,6-diphenyl-pyrylium salts[163]:



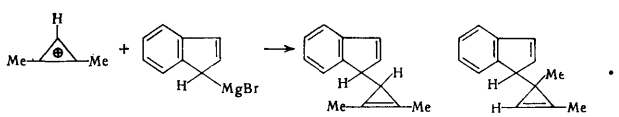
(LXXIV)

When acted upon by organometallic compounds, tropylium bromide is converted into tropylidenes (LXXIV)[156,173]. The reaction of the cyclopropenylium ion with organomagnesium and organolithium compounds proceeds

similarly [174,175]. The reaction of tropylium salts with certain organomercury compounds is interesting [170,171]:

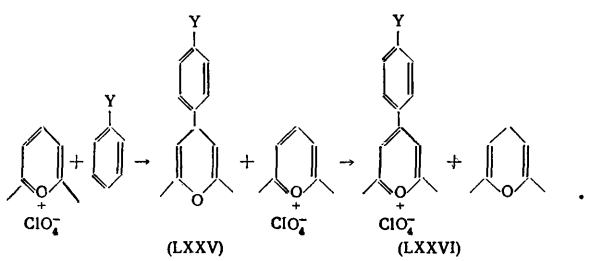


Tropylium cations react with cyclopentadienylsodium or cyclopentadienyllithium to form cyclopentadienylcycloheptatriene [156,171]. The dimethylcyclopropenylium cation reacts with indenylmagnesium bromide to form a mixture of two isomeric dimethylindenylcyclopropenes. The formation of the mixture shows that the charge of the cyclopropenylium cation is distributed among the three ring carbon atoms and is not fixed at any one of them [176]:



2. The Pyrylation Reaction

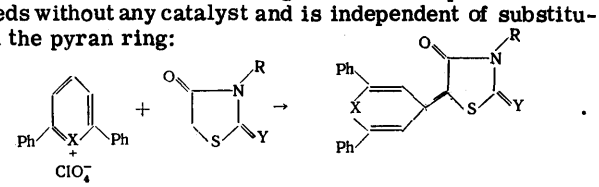
Pyrylium salts without substituents in at least one of the α- and γ-positions should presumably interact with reactive compounds to form new 2*H*- or 4*H*-pyrans [for example (LXXV)]. However, it was found [177-179] that the intermediate pyran (LXXV) splits off a hydride ion in the presence of 2,6-diphenylpyrylium perchlorate and is converted into the pyrylium cation (LXXVI) via the mechanism



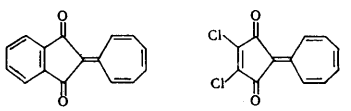
(LXXV) (LXXVI)

The elimination of a hydride ion by the pyrylium cation is possible only when there is a fairly high electron density in the γ-position of the pyran (LXXV) (higher than in the pyran whose γ-position is free). The pyrylation reaction has been extended to nucleophilic agents and heteroaromatic cations [179].

Earlier Wizinger and coworkers [165,166] carried out the condensation of thiapyrylium and flavylium salts with dimethylaniline in acetic acid in the presence of sodium acetate and Krönke and Dickore carried out the reaction in acetic anhydride [164], but these reactions have not become commonly used in the synthesis of pyrylium salts. The reaction of various 4-azolidinones with unsubstituted pyrylium salts has been investigated [180]. The process proceeds without any catalyst and is independent of substitution in the pyran ring:

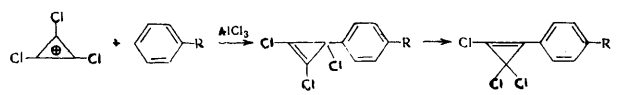


The substitution of a mobile hydrogen atom in the series of tropylium salts by the cycloheptatrienyl residue has been used extensively in the synthesis of cycloheptatriene derivatives [181]. Thus it proved possible to introduce the seven-membered ring into the molecules of various cyclic compounds [182,183]. Hafner et al. [184] and Anderson and Reploge [185] introduced the tropylium group into azulene and Kitahara et al. obtained the quinones (LXXVII) and (LXVIII) of the sesquifulvalene series with the aid of the tropylation reaction [186]:

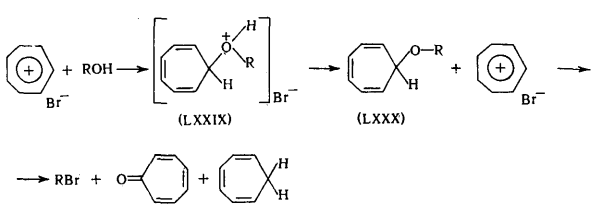


(LXXVII) (LXXVIII)

The trichlorocyclopropenylium cations enters into reactions involving electrophilic substitution of the aromatic ring (with benzene, toluene, chlorobenzene, and fluorobenzene) [187,188] of the Friedel–Crafts type:

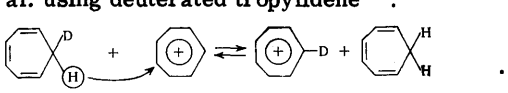


The reaction can be carried out with subsequent substitution of the three positions. Tropylium and cyclopenylium cations react with alcohols (primary, secondary, and tertiary) to form alkoxy-derivatives of tropylidene and cyclopropene [189,190]. It is believed that the first step in the reaction of the tropylium cation with alcohols is the formation of an oxonium compound (LXXIX), which readily loses a proton and is converted into an alkyl tropyl ether (LXXX). The latter interacts with a second molecule of the tropylium salt to form cycloheptatriene, tropene, and an alkyl halide [190]:

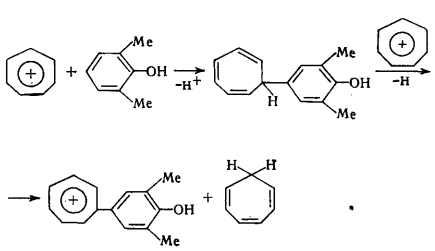


(LXXIX) (LXXX)

Kursanov et al. [191] studied the reaction of the tropylium ion with ethers. The hydride shifts in the tropylium–cycloheptatriene system have been examined in detail by Vol'pin et al. using deuterated tropylidene [192]:



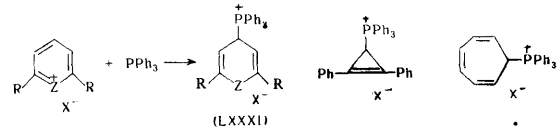
Repeated hydride shifts in this system lead to a redistribution of deuterium between tropylium and cycloheptatriene. Numerous reactions of the tropylium ion with reactive organic compounds take place with hydride ion transfer. Thus, according to van Helden et al. [193], the reaction with 2,6-dimethylphenol proceeds via the mechanism



Numerous hydride shift reactions involving the tropylium ion have been examined in detail in a monograph [194].

3. Organophosphorus Derivatives of Aromatic Cations

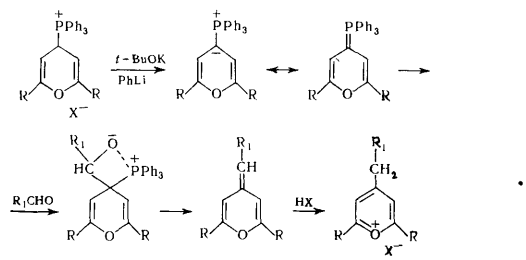
Heteroaromatic cations with a free α- or γ-position react readily and almost quantitatively with triphenylphosphine to form phosphonium salts (LXXXI).[195,196] It was found that this reaction is applicable also to tropylium and cyclopropenylium ions[197]:



(LXXXI)

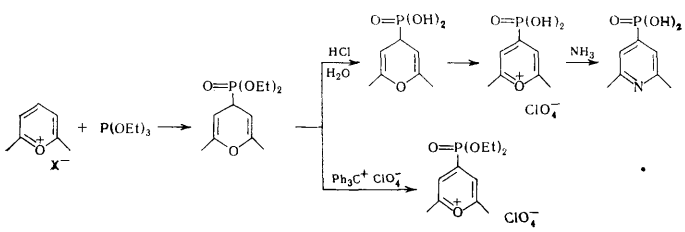
(X = ClO_4, BF_4, Br. Z = O, S, Se)

When bases are allowed to act on a suspension of these salts in ether, with cooling (to −30°C and below), phosphoranes are formed (for example, from phosphonium salts and phenyl-lithium or potassium t-butoxide); these normally react with carbonyl compounds[195]:



The synthesis of phosphonium salts and phosphoranes and the reactions of the latter with carbonyl compounds have been studied in very great detail[198]. The reaction is general and permits the variation of the carbonyl components within wide limits[199].

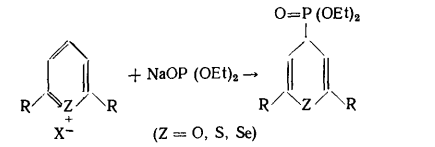
The reaction of the halides of the aromatic cations considered with triethyl phosphite, which is of the type of the Arbuzov rearrangement, has been investigated in detail[200–202]. The resulting phosphonates undergo various further reactions. For example, pyranylphosphonates (obtained from various pyrylium salts and triethyl phosphite) have been converted by acid hydrolysis into pyranylphosphonic acids and the latter have been converted by the elimination of a hydride ion into the corresponding pyrylium salts with a phosphonic acid residue. The recyclisation of these salts led to pyridylphosphonic acids:



On the other hand, pyranylphosphonate is readily converted into pyrylylphosphonate. The reaction is applicable to any charged aromatic systems but cyclopropenyl- and cycloheptatrienyl-phosphonic acids and their esters could not be converted into the corresponding salts.

The Arbuzov rearrangement in the series of aromatic cations is carried out under fairly severe conditions, which gives rise to side reactions. This rearrangement is applicable only to the corresponding chloride, bromide, and iodide salts. However, the latter are difficult to obtain, hygroscopic, and frequently unstable on storage.

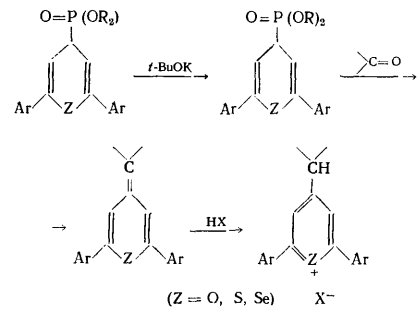
These advantages can be avoided by carrying out the Michaelis–Becker reaction of the above compounds with the sodium salt of diethyl phosphite[203]:



(Z = O, S, Se)

The resulting phosphonates are converted into phosphonic acids and into pyrylium salts with phosphorus containing substituents[204], as described above.

Phosphonates derived from various aromatic cations and obtained by the Michaelis–Becker reaction interact with potassium t-butoxide to form coloured reactive carbanions. The latter readily react *in situ* with various carbonyl compounds to form ultimately arylidene or alkylidene derivatives of pyrans and similar compounds[204,205]. The following reaction mechanism has been proposed:

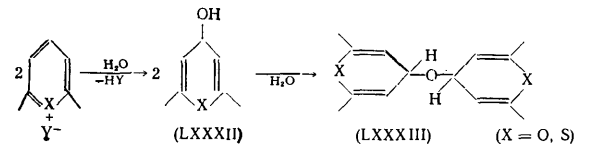


(Z = O, S, Se) X^-

This is probably the simplest and most convenient method for the introduction of an exocyclic double bond into pyran, thiapyran, selenapyran, and other cyclic systems based on pyrylium, flavylium, xanthylium, tropylium, cyclopropenylium, and other salts.

4. Interaction with Certain Inorganic Nucleophilic Agents

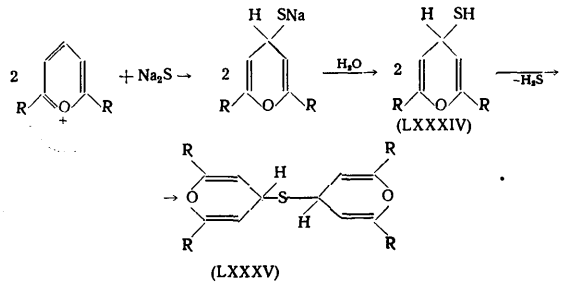
Pyrylium and thiapyrylium salts with a free γ-position are converted in the presence of organic bases (pyridine, hexamethylenetetramine) into di-($\alpha\alpha'$-diphenyl-γ-pyranyl) or di-($\alpha\alpha'$-diphenyl-γ-thiapyranyl) ether (LXXXIII).[206] The reaction most probably proceeds via the intermediate formation of 4-hydroxy-2,6-diphenylpyran (LXXXII):



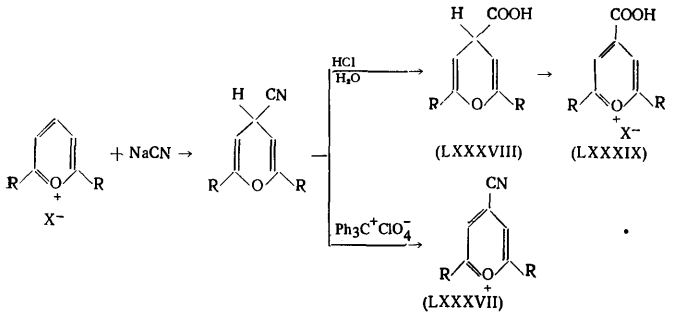
(LXXXII) (LXXXIII) (X = O, S)

Organic bases can be replaced by aqueous sodium bicarbonate. This method for the conversion of pyrylium salts into dipyranyl ethers is similar to the formation of ditropyl[173], dicyclopropenyl[10], and dixanthyl[207] ethers from the corresponding salts. It is interesting that the reaction of 2,6-diphenylpyrylium perchlorate with sodium sulphide in an aqueous ethereal medium does not result in the formation of the corresponding dipyranyl sulphide analogous to diparanyl ether[206] and ditropyl sulphide[173].

It was found that the mercaptopyran (LXXXIV) is formed under these conditions and only on heating in inert solvents does it split off hydrogen sulphide and is converted into dipyranyl sulphide (LXXXV):[208]

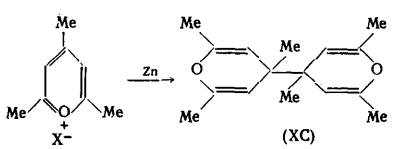


The reaction of γ-unsubstituted pyrylium salts with potassium cyanide in an aqueous ethereal medium leads to the corresponding γ-cyanopyrans (LXXXVI). On being refluxed with triphenylmethyl perchlorate the latter split off a hydride ion and are converted into γ-cyanopyrylium salts (LXXXVII).[208] On the other hand, hydrolysis of pyrans by dilute hydrochloric acid yields carboxypyrans (LXXXVIII), which can be converted into carboxypyrylium salts (LXXXIX):



The interaction of KCN with 2,4,6-trisubstituted pyrylium ions has been studied in a series of pyrylium salts[104], but the possibility of the conversion of the cyanopyrans formed initially into carboxypyrans or especially into cyano- and carboxy-pyrylium salts is ruled out in this case. The reaction of tropylium and diphenylcyclopropenylium salts with potassium cyanide leads to the formation of 7-cyanocycloheptatriene[7,156] and 3-cyano-1,2-diphenylcyclopropene respectively[8,175]. The reaction of tropylium salts with ammonia has been studied in detail. Depending on the component ratio and the reaction conditions, mono-, di-, and tri-tropylamines or their mixtures can be formed[156]. It was expected that γ-unsubstituted pyrylium salts would react similarly. However, pyridine was obtained unexpectedly[208]. Aminopyran could not be obtained either by reaction with sodamide or with potassium phthalimide. In the latter case a phthalimide derivative of pyran is readily obtained but Gabriel hydrolysis (and hydrazinolysis) leads to appreciable charring[208].

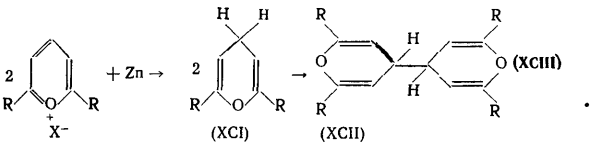
Balaban et al.[209] showed that, when metallic zinc is allowed to react with 2,4,6-trimethylpyrylium perchlorate, the salt undergoes one-electron reduction with formation of 2,2',4,4', 6,6'-hexamethyl-4,4'-bispyran (XC):



The same product was obtained by the reaction of the disodium salt of the cyclooctatetraene dianion with trimethylpyrylium perchlorate[210].

On heating with metal powders (magnesium, copper, zinc, and aluminium) in organic solvents (alcohol and acetonitrile), triarylpyrylium salts are reduced with formation of intensely coloured species—stable free radicals[211].

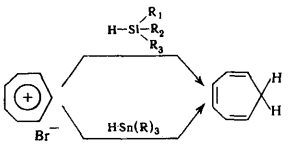
When this reaction is carried out with γ-unsubstituted pyrylium salts in a polar solvent, the radicals (XCI) formed recombine and the bipyranyls (XCII) are obtained[212]:



The corresponding dimers have been synthesised from flavylium salts and their 3-alkyl- or 3-aryl-derivatives by the reaction with zinc dust in acetonitrile[213]. When xanthylium salts react with dispersed silver, stable radicals are also formed[214]. The synthesis of bitropyl (XCIII) using zinc dust and other metal powders has been described for the series of tropylium salts[173]. The tropylium ion can be reduced to bitropyl by transition metal complexes[171]. The analogy between pyrylium salts and non-benzenoid aromatic cations in the formation and recombination of radicals is completed by the cyclopropenylium ion[215].

The reduction of pyrylium salts by sodium tetrahydroborate leads to the formation of mixtures of substituted 4*H*-pyrans and pentadienones[216,217]. On reduction with sodium tetrahydroborate in alcohol, flavylium perchlorate is also converted into dimers[218].

When tropylium bromide is acted upon by lithium tetrahydroaluminate or sodium tetrahydroborate (as hydride ion donors), cycloheptatriene is formed. This property of tropylium as a hydride ion acceptor has been used to investigate hydride shifts[219]. It was found that Si-H and Sn-H bonds can also be broken heterolytically under the influence of tropylium bromide[220]:



The cyclopropenylium cation is reduced by lithium tetrahydroaluminate to cyclopropene[174].

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