SYNTHESIS AND PROPERTIES OF 1,3-DIOXOLANIUM SALTS (REVIEW)

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Methods for the synthesis of 1,3-dioxolanium salts – a new class of carboxonium cations that are finding application in organic synthesis – and their structure and properties are examined.

1,3-Dioxolanium salts are a peculiar class of nonaromatic carboxonium compounds. The presence of a stabilized carbonium ion makes dioxolanium salts convenient models for the study of the reactivities and behavior of carbonium ions. There is also no doubt about the preparative value of 1,3-dioxolanium salts, which, owing to their high activity with respect to various nucleophilic reagents, can be used as effective alkylating, formylating, and acylating agents.

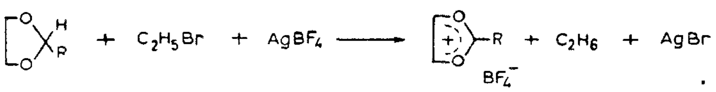
The chemistry of 1,3-dioxolanium salts is a relatively new and little-studied field. The first information regarding the possibility of the development of 1,3-dioxolanium ions as intermediates in solvolysis reactions of acetoxybromobutanes appeared in 1942 [1-3], but these substances were obtained and isolated in pure form only in 1955-1960 by Meerwein and co-workers [4-9].

A recently published review [10] encompasses information regarding 1,3-dioxolanium salts through 1970 inclusively. However, whereas methods for the synthesis of dioxolanium salts have been presented relatively completely, the properties and transformations of this class of compounds have been elucidated concisely. In addition, the review in [10] does not include the results of quite extensive studies on the synthesis and properties of dioxolanium salts carried out by Soviet chemists.

The present review is intended to supplement, correlate, and systematize the available information on the methods for the synthesis of 1,3-dioxolanium salts and their properties.

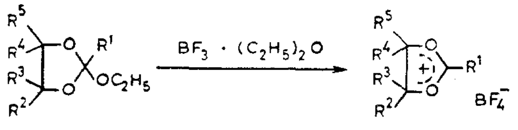
Methods for the Synthesis of 1,3-Dioxolanium Salts

From 1,3-Dioxolanes. Cyclic acetals are effective hydride-ion donors and can be easily converted to the corresponding 1,3-dioxolanium salts [4, 7].



Triethyloxonium [8], arenediazonium [7], triphenylcarbonium [8, 11-13], and 7-norborandienylium [11] tetrafluoroborates and acetyl perchlorate [14] are used as hydride-ion acceptors.

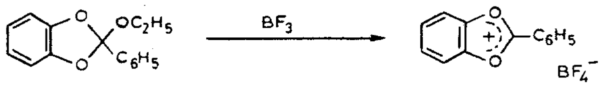
A widely used method for the preparation of 1,3-dioxolanium salts is the reaction of 2-ethoxy-1,3-dioxolane and its derivatives with boron trifluoride etherate [9, 15].



$R^1 = H, CH_3, C_2H_5, C_6H_5$; $R^2 = R^3 = R^4 = H, CH_3$; $R^5 = H, CH_3, CH{=}CH_2$

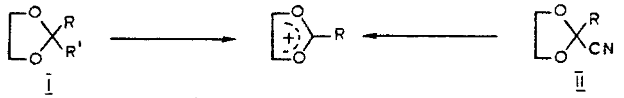
Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 869-882, July, 1975. Original article submitted August 12, 1974.

This method was also used to obtain 4,5-tetramethylene- [12] and benzo- and 2,3-naphtho-1,3-dioxolanium salts [16]



Antimony pentachloride (in methylene chloride at − 25°), $H_2SO_4 \cdot H_2O$ (at − 70°), diethoxy- and triphenylcarbonium tetrafluoroborate [8, 11], and perchloric acid (in acetic anhydride) [17] are used to cleave the alkoxy group.

2-Methyl- and 2-phenyldioxolanium salts are obtained by treatment of cyclic ketals (I) [18] and 2-cyano-1,3-dioxolanes (II) [8] with Lewis acids.

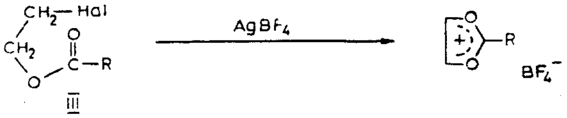


R = CH_3, C_6H_5 ; R' = CH_3, C_2H_5, iso-C_3H_7

Cyclization of Substituted Esters. β-Ethoxyethyl acetate is cyclized to the corresponding 1,3-dioxolanium salt on heating with $Et_3O^+BF_4^-$; β-ethoxyethyl benzoate is cyclized at − 30° in the presence of $SbCl_5$ [9].

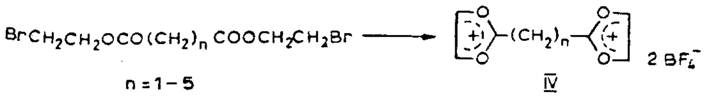
The conversion of β-hydroxy-, β-acetoxy-, and β-methoxyethyl esters to 2-alkyl- or 2-aryldioxolanium salts, which occurs in FSO_3H at room temperature [19, 20], has been described.

Cyclization of β-haloethyl esters of carbonylic acids (III) in the presence of $BF_3 \cdot Et_2O$, $SbCl_5$, and $AgBF_4$ [6, 9, 21] is widely used for the synthesis of 1,3-dioxolanium salts (in 50-80% yields).

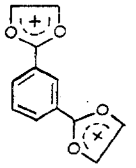


This method has found application for the preparation of 2-amino-, vinyl-, alkyl-, aryl- [19, 20, 22, 23], and 4,5-tetramethylenedioxolanium [13,24] tetrafluoroborates and hexachloroantimonates and analogous salts in the steroid series [25, 29].

Bisdioxolanium salts IV [30] are formed on treatment of bis(2-bromoethyl) esters with anhydrous $AgBF_4$ in CH_2Cl_2:



Di- and trications V-VII were synthesized from 2-bromoethyl phthalates and trimesitates [19, 20]:



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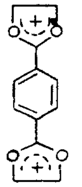
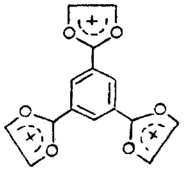
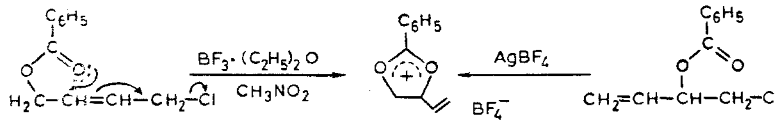


VI



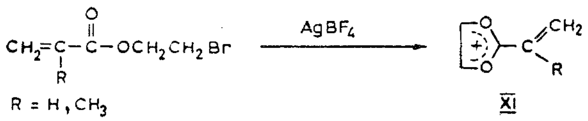
VII

The rearrangement of 4-chloro-2-butenyl benzoate (VIII) to give 4-vinyl-2-phenyl-1,3-dioxolanium salt IX, which was also obtained from β-chloroethyl ester X [15, 31], has been described



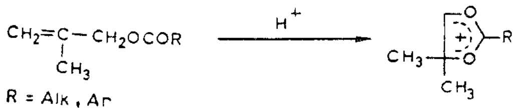
VIII IX X

2-Vinyl- and 2-isopropenyl-1,3-dioxolanium tetrafluoroborates (XI) are obtained by cyclization of 2-hydroxyethyl and 2-bromoethyl esters of acrylic and methacrylic acids in FSO_3H or with $AgBF_4$ in methylene chloride [32, 33].



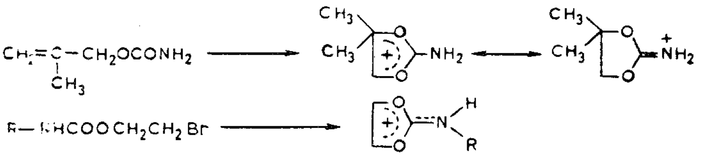
XI

1,3-Dioxolanium cations are formed quantitatively on protonation of methylallyl esters with 60-96% H_2SO_4 and FSO_3H [34-36].

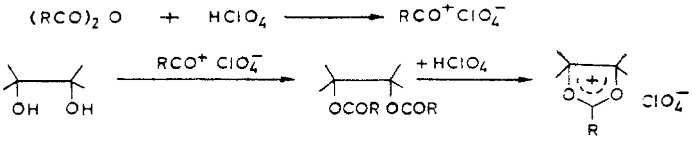


Allyl acetate gives only 30% 2,4-dimethyl-substituted dioxolanium salts, whereas the acetates and benzoates of secondary allyl alcohols do not form dioxolanium cations at all [34].

Cyclization of carbamates has made it possible to obtain 2-amino-1,3-dioxolanium salts [34, 37]

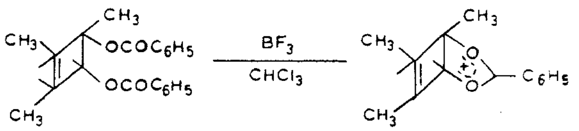


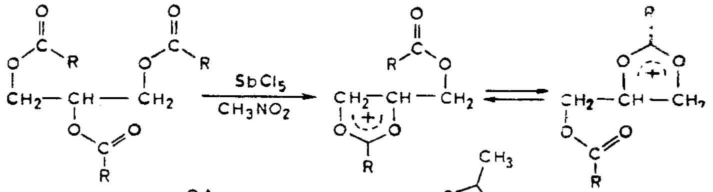
The simplest method for the synthesis of 2-alkyl-1,3-dioxolanium salts is acylation of α-glycols with aliphatic acid anhydrides in the presence of 70% perchloric acid (the yields are 65-95%) [38, 39].

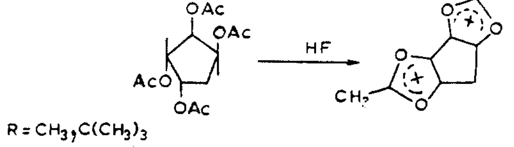


Pinacolone rearrangement does not occur under cyclization conditions, inasmuch as the rate of the rearrangement is considerably less than the rate of acylation of the hydroxy group by the acyl cation [38, 39].

The later-described cyclization of esters of di-, tri-, and tetra-atomic alcohols is a variant of this method [40-48].







The synthesis of O-alkylglycosides from acetyl halides, silver perchlorate, and aliphatic alcohols also apparently proceeds through the intermediate formation of 1,3-dioxolanium salts [49, 50].

Spectral Characteristics of 1,3-Dioxolanium Salts

Of the spectral characteristics of 1,3-dioxolanium salts, PMR spectroscopic data are most frequently presented in the literature. A number of studies of the effect of substituents on the chemical shifts of the protons of the 1,3-dioxolanium ring have been published [19, 20, 25, 30, 40, 41].

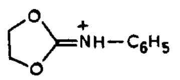
The spectra of a number of dioxolanium salts with various substituents in the 2 position are characterized by a singlet at δ 4.98-5.70 ppm for the equivalent 3- and 4-H methylene protons. The proton in the 2 position in the 4-substituted derivative gives a signal at δ 9.40 ppm. More detailed data on the PMR spectroscopy of 1,3-dioxolanium salts are summarized and presented in detail in [10].

The molecular spectra of 1,3-dioxolanium salts have been investigated only in the case of a few representatives [25, 38, 39, 51-53]. Thus the IR spectra of 2-alkyl-1,3-dioxolanium perchlorates contain two intense absorption bands at 1529-1536 and 1495-1508 cm^{-1}, which were assigned to the vibrations of the $O{=}\overset{+}{C}{=}O$ fragment of the dioxolanium cation. When a styryl substituent is introduced into the 2 position, PU because of conjugation with the latter, the absorption bands of the dioxolanium ring are shifted as compared with the absorption bands of 2-alkyl-substituted dioxolanium salts to 1548-1572 and 1500-1520 cm^{-1}.

The data from electronic spectroscopy are also extremely limited. Slight absorption at no higher than 220 nm was observed for 4,4,5,5-tetramethyl-1,3-dioxolanium ion in H_2SO_4 [10]. The UV spectra of 2-aryl- and 2-styryldioxolanium salts also contain another absorption maximum in the shortwave region at 280-300 nm [22, 51]. Intense absorption in the visible region of the spectrum (400-427 nm) is observed when CH_3O, 3,4-(CH_3O), 3,4-CH_2O_2, and HO are introduced in the para position of the aromatic ring, whereas intense absorption is observed at 500 nm when a p-$N(CH_3)_2$ substituent is introduced in the para position.

Reactivities of 1,3-Dioxolanium Salts

Dioxolanium salts are representatives of stable heterocyclic carbonium ions. Some thermodynamic and kinetic data attesting to the high stabilizing capacity of oxygen atoms adjacent to a carbon atom and the considerable stability of 1,3-dioxolanium ions, for which, for example, the heat of formation from methylallyl esters is ~ − 30 kcal/mole (for comparison, the heat of formation of the extremely stable diphenylmethyl carbonium ion from 1,1-diphenylethylene is − 15 kcal/mole), are presented in the review in [10]. From these same data one can draw several conclusions regarding the effect of a substituent in the 2 position of the heterorings on the stability of the 1,3-dioxolanium ion. Thus replacement of a hydrogen atom of the methyl group (+I effect) leads to an increase of 3.6 kcal/mole in the stability. A large effect (5.4 kcal/mole) is achieved when an NHC_6H_5 substituent is introduced, and this is probably explained by the contribution of the resonance form

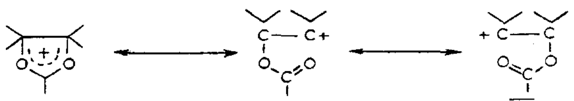


In the case of 2-aryl-1,3-dioxolanium cations the stability can be increased by the introduction of electron-donor substituents in the aromatic ring [10].

One must also note that deuterium exchange of the 2-CH_3 group does not occur in 2-methyl-1,3-dioxolanium ions in strong acids [10, 34], and this once again indicates the effective stabilization of the charge by two heteroatoms.

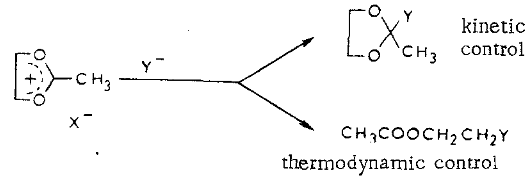
On turning to an examination of the properties and transformations of 1,3-dioxolanium salts we must first of all note the ambident character of the latter, which is manifested in reactions of dioxolanium salts with nucleophilic reagents, the attack of which is realized at the C-2 or C-4 atoms of the heteroring.

The dual reactivity of these compounds is a consequence of delocalization of the positive charge, which can be described by mesomeric structures XII-XIV:



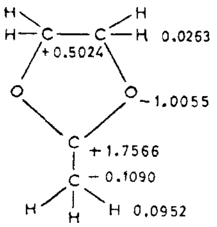
XII XIII XIV

The dual nature of cyclic carboxonium ions was first detected by Meerwein [9]:



The character of the final reaction products is determined by the strength of the bond arising as a result of primary attack on the dioxolanium cation by the nucleophile and by the capacity of the product to undergo dissociation at this bond.

The addition of nucleophile Y^- occurs most readily in the 2 position of the heteroring, which has the lowest electron density:

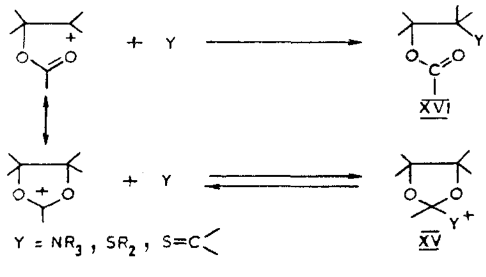


If the product obtained in this case is sufficiently stable and reverse dissociation to the cation does not occur under the reaction conditions, the kinetic pathway will be the preferred one. If, however, addition in the 2 position is reversible, the probability of the formation of the product of thermodynamic control increases.

In addition, the direction of the reaction depends on the energy of the cation itself, the nature of the nucleophile, the temperature, the reaction time, and the solvent [10].

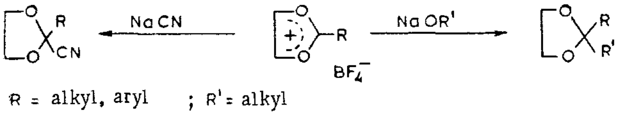
A relationship between the direction of action of the attacking anion and its basicity is observed in the case of anionoid nucleophiles. Thus the stable slightly basic anions of acids (CH_3COO^-, TsO^-, Cl^-, Br^-, and I^-), for which $pK_a < \sim 8\text{-}6$, give products of opening of the dioxolanium ring. On the other hand, strong bases (HO^-, RO^-, ArO^-, CN^-, and R^-), for which the pK_a values of the conjugate acids > 8-9, add in the 2 position of the ring.

Neutral nucleophilic molecules (triethylamine, pyridine, tetrahydrothiophene, and thiourea), in the case of which the primary adducts are cations XV, which are capable of undergoing ready dissociation to the starting components, as a rule, form the thermodynamically more favorable ring cleavage products XVI:



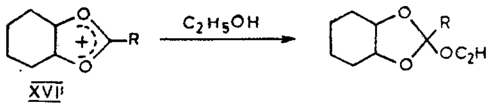
All of the presently known types of reactions of 1,3-dioxolanium salts are examined below in concrete examples.

Nucleophilic Addition Reactions in the 2 Position of the 1,3-Dioxolanium Ring. Dioxolanium salts react readily at room temperature with sodium alkoxides [9, 22] and with sodium cyanide [9] on prolonged stirring (48 h) in methylene chloride and acetonitrile (1 : 1) to give the corresponding 2-alkoxy- and 2-cyano-1,3-dioxolanes:



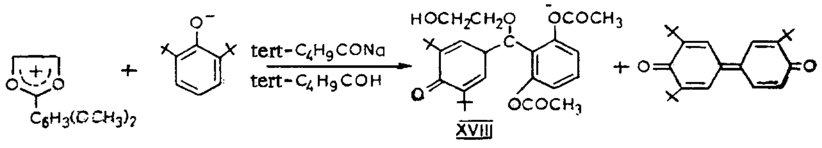
4,5-Benzo-, 4,5-naphtho- [16], and 4-vinyl-1,3-dioxolanium [15] tetrafluoroborates react similarly with sodium ethoxide and methoxide.

The addition of an alkoxy group also occurs on treatment of 4,5-tetramethylene-1,3-dioxolanium salts (XVII) [54] and derivatives of a number of carbohydrates [29] with lower alcohols.

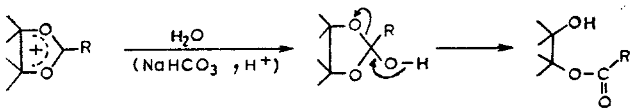


Unsubstituted (in the 4 and 5 positions) 1,3-dioxolanium salts undergo cleavage on heating with alcohols to give β-alkoxyethyl esters of carboxylic acids [9, 22]

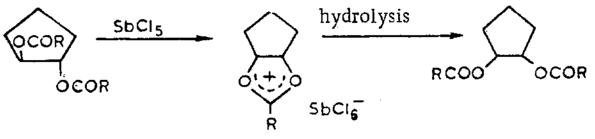
In contrast to alkoxides, 2,6-di-tert-butylphenoxide attacks the C-2 atom with the para carbon atom of the benzene ring [22]. The presence in the IR spectrum of an OH band at 3400 cm^{-1} indicates that prototropic opening of the dioxolanium ring to give quinomethane XVIII occurs in this case:



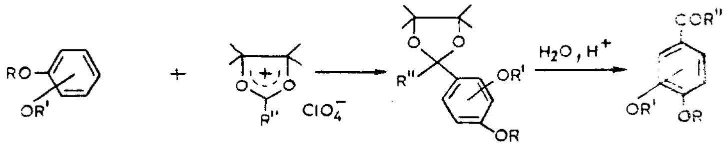
The addition of water is also accompanied by prototropic opening of the heteroring in all cases [9, 16, 22, 29, 38, 39, 51, 54]:



This reaction is of preparative value, inasmuch as it is a convenient method for the conversion of trans isomers to cis isomers [40-43]:



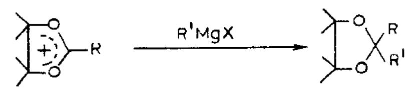
The reaction of 1,3-dioxolanium salts with active aromatic compounds, which takes place when the components are refluxed in glacial acetic acid, is of considerable interest [17, 55, 56]:



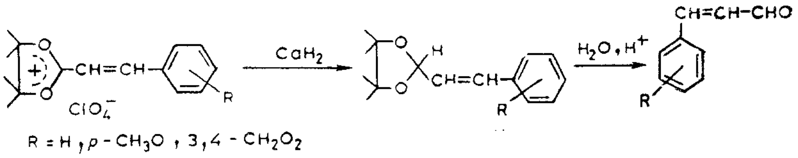
The 1,3-dioxolanes formed in this case are readily converted to the corresponding aldehydes and ketones, i.e., aromatic compounds are acylated on reaction with 1,3-dioxolanium salts.

Some heterocyclic compounds (indole) also react similarly with dioxolanium salts [55].

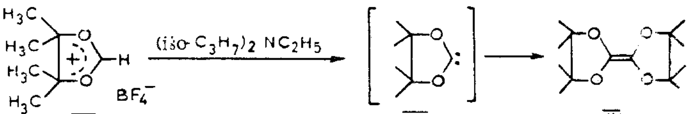
Organomagnesium compounds add extremely readily to the 2 position of the dioxolanium cation [16, 52]:



When 2-(β-aryl)vinyl-1,3-dioxolanium perchlorates are refluxed in chloroform with metal hydrides, the hydride ion adds after 5 min to give cyclic acetals of substituted cinnamaldehydes, the hydrolysis of which gives free unsaturated aldehydes (in 55-70% yields) [57]:

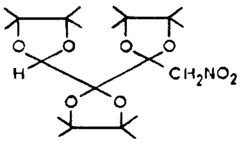


The conversion of 4,4,5,5-tetramethyl-1,3-dioxolanium tetrafluoroborate (XIX) to its "dimer" (XX), which proceeds through intermediate carbene XXI on treatment of the salt with diisopropylethylamine, has been described [12]:



XIX XXI XX

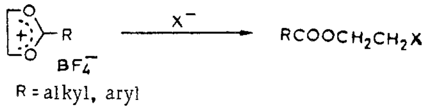
It has been proposed that this pathway be used to obtain alkenes from cis-glycols, but the carbene did not decompose spontaneously to CO_2 and tetramethylethylene but reacted with the starting cation.



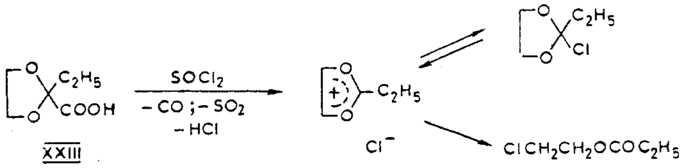
XXII

When nitromethane was used as a solvent, a compound to which structure XXII was assigned was isolated. It may be formed by reaction of salt XIX and dimer XX with subsequent attack of acinitromethane on the resulting carbonium ion.

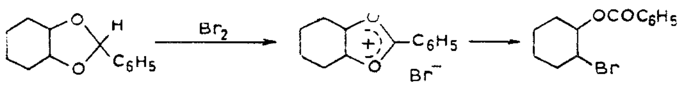
Reactions in the 4 Position Accompanied by Opening of the Dioxolanium Ring. β-Haloethyl esters of the corresponding carboxylic acids were isolated (in 60-100% yields) on treatment of a solution of the dioxolanium salt in acetonitrile with lithium chloride [9], sodium bromide [22, 58], or sodium iodide [9]:



The rearrangement of acid XXIII, which occurs in the presence of thionyl chloride, has been described [29, 59]:

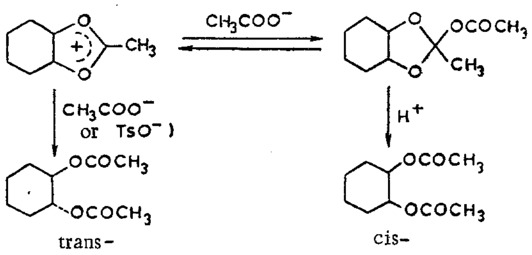


2-Phenyl-4,5-tetramethylenedioxolane is also converted to a β-bromo-substituted ester under the influence of bromine [29]:

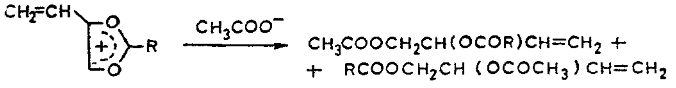


These reactions confirm that the β-haloethyl esters are thermodynamically more stable than the dioxolanium halides.

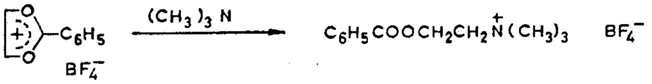
Similar opening of the dioxolanium ring also occurs in the case of sodium acetate and p-toluenesulfonate [29, 54, 60, 61]:



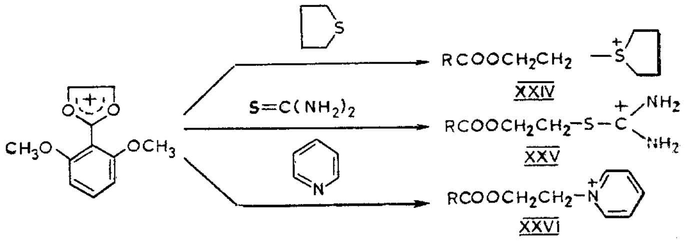
4-Vinyldioxolanium tetrafluoroborate reacts with sodium acetate to give a mixture of isomeric esters [15]:



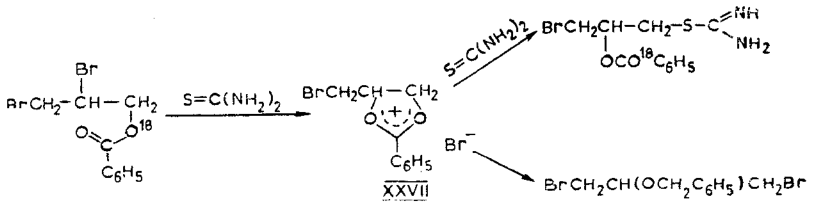
In acetonitrile at 0°, the 2-phenyldioxolanium ion adds trimethylamine to give a quaternary ammonium salt [9]:



The possibility of alkylation of the nitrogen and sulfur atoms in nucleophilic molecules by the 1,3-dioxolanium cation has been demonstrated [22]. While attempts to alkylate diphenyl sulfide and benzyl mercaptan were unsuccessful, tetrahydrothiophene, thiourea, and pyridine react with opening of the dioxolanium ring to give, respectively, new sulfonium (XXIV), isothiuronium (XXV), and pyridinium (XXVI) salts (in 50-80% yields).

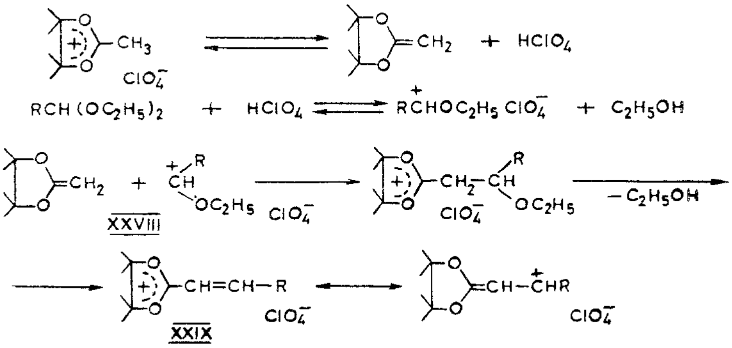


The reaction of 2,3-dibromopropyl benzoate with thiourea proceeds through 1,3-dioxolanium ion XXVII, which is opened at C-5 by nucleophilic attack [62]:



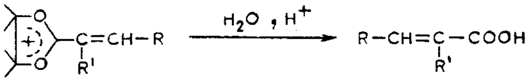
Reactions of the Alkyl Groups in 1,3-Dioxolanium Salts. The presence of a positive charge on the meso carbon atom in 1,3-dioxolanium salts activates the alkyl group in the 2 position of the heteroring and is responsible for the possibility of condensation reactions with various compounds. 2-Methyl- and 2-ethyl-substituted dioxolanium perchlorates condense very readily with acetals of aromatic and heterocyclic aldehydes (in 80-95% yields) [51, 57] (the aldehydes themselves do not undergo this reaction).

The mechanism of this reaction is evidently analogous to the mechanism of similar types of condensations in a number of quaternary salts of nitrogen- or oxygen-containing heterocycles. The fact that electron-donor substituents in the aryl ring of the acetal, which stabilizes intermediate ethoxy carbonium ion (XXVIII), increase the yields of reaction products to 90-98%, whereas the reaction does not proceed at all with p-nitrobenzaldehyde acetal, is in agreement with the mechanism presented on the next page.



R = aryl, hetaryl

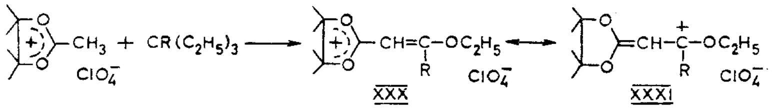
α,β-Unsaturated aromatic and heterocyclic acids are obtained in quantitative yields by hydrolysis of 2-(1-alkenyl)-1,3-dioxolanium salts:



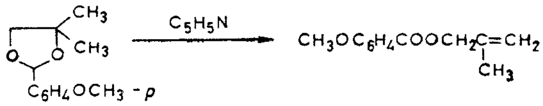
$R' = H, CH_3$

Ketals undergo condensations with 1,3-dioxolanium salts with much greater difficulty, and the yields of β-alkyl-substituted unsaturated acids are very low [51, 52].

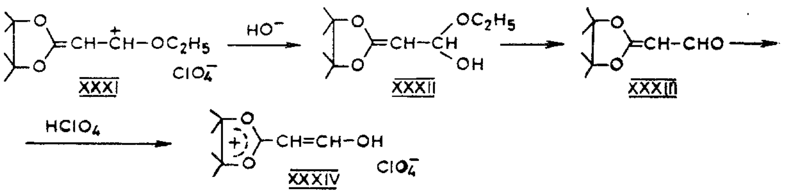
In addition to acetals and ketals, ortho esters react readily with 2-alkyl-1,3-dioxolanium salts [53]. The reaction takes place on brief heating of equimolecular amounts of the components in excess acetic anhydride, and 2-β-ethoxyvinyl derivatives XXX, the properties of which are examined below, are isolated in 62-87% yields.



The only case involving the participation in the reaction of the 4-methyl group of a 1,3-dioxolanium salt is presented in [10]:

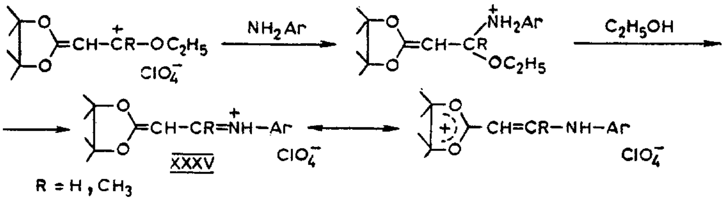


Reactions of the Alkenyl Groups of 2-Alkenyl-1,3-dioxolanium Salts. As we have already pointed out above, 1,3-dioxolanium salts react exceptionally readily with water with opening of the heteroring. However, the behavior of the 2-β-ethoxyvinyl derivative in this sort of reaction differs substantially. Under the influence of aqueous alkali, the attack of the nucleophile is directed to the positively charged β-carbon atom of the ethoxyvinyldioxolanium salt (mesomeric form XXXI) [53]:



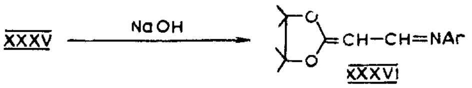
It follows from the results of quantum-mechanical calculations of the charges for 2-β-methoxyvinyl-1,3-dioxolanium ion [53] that the ring carbon atom is the most active center with respect to nucleophilic attack. However, the difference in the nucleophilic reactivity indexes (for which the electron density in the boundary MO should serve as a characteristic) between this carbon atom and the β-carbon atom is slight. Inasmuch as the β-carbon atom is sterically shielded to a lesser extent, preferable reaction with transfer of the reaction center to precisely this carbon atom becomes possible. The resulting addition product (XXXII) is stabilized by splitting out of a molecule of alcohol to give α,β-unsaturated aldehyde XXXIII, which on treatment with anhydrous perchloric acid is readily protonated and converted to 2-(β-hydroxyvinyl)dioxolanium salt XXXIV.

2-(β-Ethoxy)vinyl-1,3-dioxolanium perchlorates also react with amines at the β-carbon atom of the salts, during which the ethoxy group is exchanged by an amino group to give 2-(β-amino)vinyldioxolanium salts (XXXV) in 80-98% yields [53].

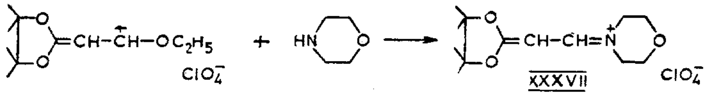


Aromatic amines, amino acids, sulfanilamides, and urea undergo this reaction.

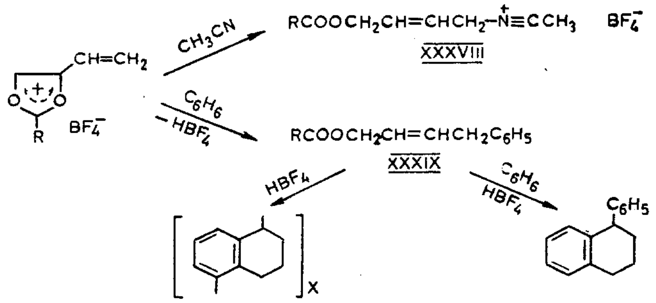
When 2-(β-amino)vinyl derivatives of 1,3-dioxolanium salts are treated with alkali, perchloric acid is split out to give the corresponding Schiff bases (XXXVI):



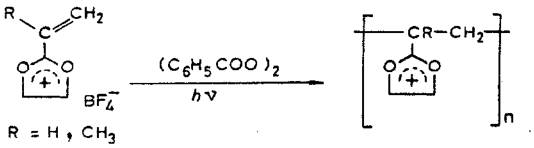
In aprotic solvents (chloroform, nitromethane), 2-(β-ethoxy)vinyl-substituted 1,3-dioxolanium salts react with aliphatic amines (N,N-diethylamine, piperidine, morpholine, and guanidine) to give 2-(β-N,N-dialkylaminovinyl)-1,3-dioxolanium perchlorates (XXXVII) [52, 53]:



The transformations of 1,3-dioxolanium salts containing a vinyl substituent in the 4 position of the heteroring are noteworthy. Thus 4-vinyl-1,3-dioxolanium tetrafluoroborate reacts with acetonitrile to give quaternary nitrilium salts XXXVIII. This same salt alkylates benzene, toluene, and anisole [15] to give the 4-aryl-2-butenyl ester (XXXIX) of a carboxylic acid, which is then converted to a 1-phenyltetralinederivative.



Patents [32, 33] have been obtained for the synthesis of poly(2-vinyl)- and poly(2-isopropenyl-1,3-dioxolanium) tetrafluoroborates:



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