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

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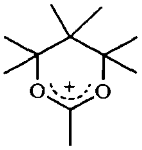
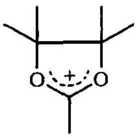
Syntheses, structures, spectral characteristics, and chemical properties of 1,3-dioxanium salts are reviewed.

Salts of 1,3-dioxanium and 1,3-dioxolanium are unique class of nonaromatic cyclic carbonium compounds that have a positive charge on the *meso*-carbon atom of the $O{-}C^{+}{-}O$ fragment. The presence of the stabilized carbocation makes acyloxonium salts as convenient models for studying the reactivity and behavior of carbenium ions. Salts of 1,3-dioxolanium have been studied more than those of 1,3-dioxanium. Until recently, this was due to their greater stability and convenient synthetic method by acylation of pinacone hydrate with acylium perchlorates [1]. Recent reports indicate that the reactivity of salts with similar structures differ depending on the presence and position of substituents in the five- or six-membered rings. Salts of 1,3-dioxanium are preferred over those of 1,3-dioxolanium.





The review by Pittman *et al.* [2] on nonaromatic 1,3-heterocarbenium ions (1,3-dioxolanium, 1,3-dioxanium, 1,3-oxathiolanium, 1,3-thiolanium, 1,3-thianium, 1,3-oxathianium, 1,3-thiazolinium, 1,3-oxazolinium) contains data on 1,3-dioxanium salts only up to 1970 inclusive. Data concerning the salts of 1,3-dioxanium and 1,3-dioxolanium have recently been significantly expanded and reviewed [1]. Therefore, the aim of the present review is to supplement, generalize and systematize existing data on syntheses, structures, spectral characteristics and properties of 1,3-dioxanium salts. Certain new data on 1,3-dioxolanium salts are included for comparison.

SYNTHESIS OF 1,3-DIOXANIUM SALTS

1,3-Dioxanium cations were considered to be unstable intermediates in the chemistry of oxygen-containing compounds for a long time [3-9].

From 1,3-dioxanes. For the first time in 1958 Meerwein successfully isolated crystalline 1,3-dioxanium salts, the carbonium system of which was stabilized by an inorganic anion. Thus, he subjected the starting reactant 2-ethoxy-4-methyl-1,3-dioxane to the action of an acceptor $BF_3 \cdot Et_2O$ or $SbCl_5$ [9].

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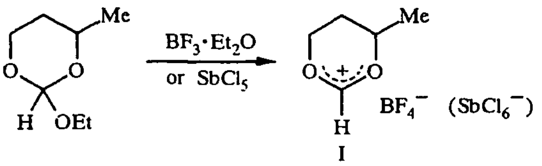
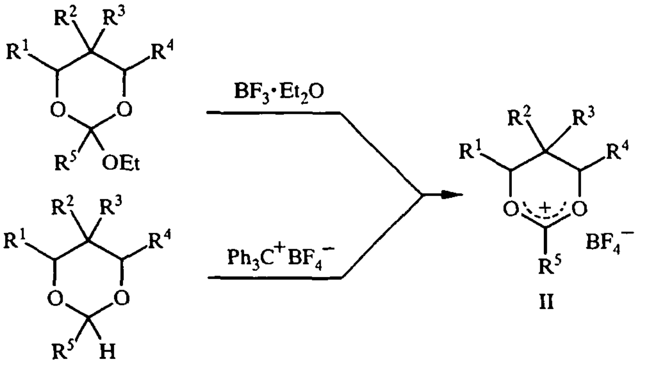


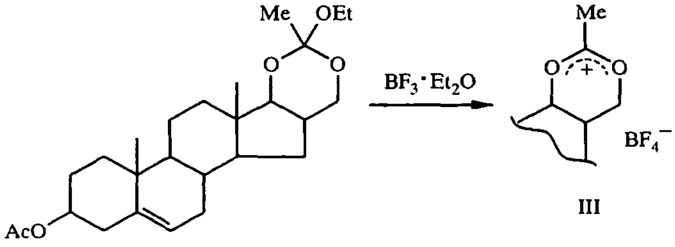
The salts were later synthesized using 1,3-dioxanes (cyclic acetals, ketals, orthoethers) by removing hydride ion or alkoxy group from ring atom $C_{(2)}$ using such reagents as Ph_3C^+, Et_3O^+, EtBr + $AgBF_4$, $SbCl_5$, and BF_3 [10-13].

Schneider *et al.* used the Meerwein method to synthesize 2-methyl- and 2-phenyl-substituted 1,3-dioxanium salts (II) [10-12]. Hydride ion is effectively removed by tritylcarbenium cation ($Ph_3C^+BF_4^-$). The yields of dioxanium salts (II) were best for $R^1 = R^4 = H$ and $R^2 = R^3$.

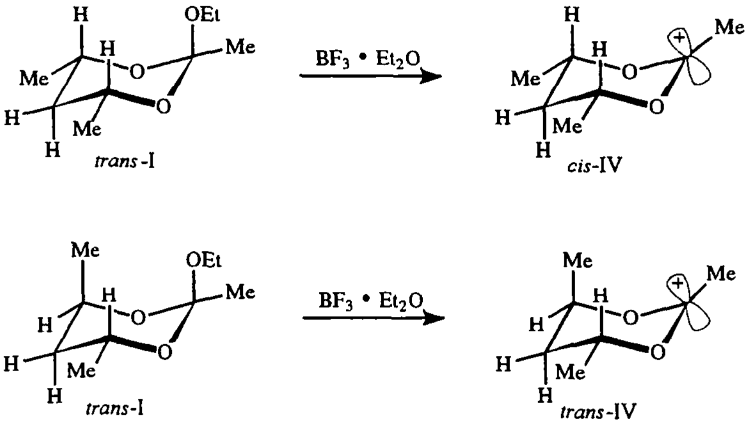


$R^1 = R^2 = R^3 = R^4 =$ H, Me, Et, Pr, Bu; $R^1 = R^2 =$ —$(CH_2)_4$—; $R^5 =$ Me, Ph

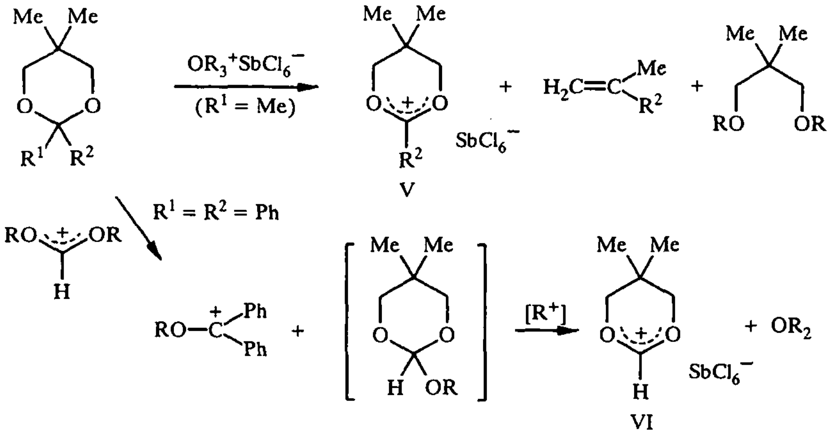
Schneider *et al.* when studying steroids obtained the stable acyloxonium ions (III) [13, 14].



Itoh *et al.* [15] used the Meerwein reaction to prepare stereoisomeric 2,4,6-trimethyl-1,3-dioxanium tetrafluoroborates (IV).

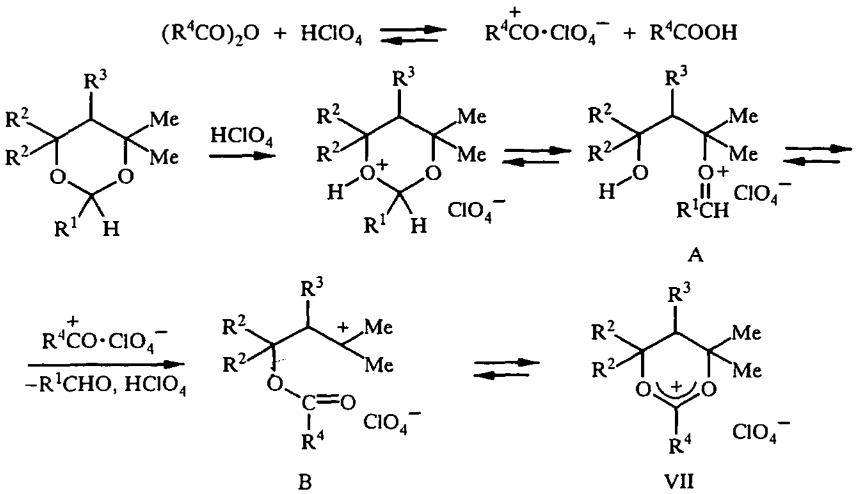


Kabuss proposed to prepare the 1,3-dioxanium salts (V) and (VI) by interaction of ketals with oxonium ions $[HC(OEt)_2^+ \cdot SbCl_6^-, Et_3O^+ \cdot SbCl_6^-]$ [16].



R^2 = Me, Ph, R = alkyl

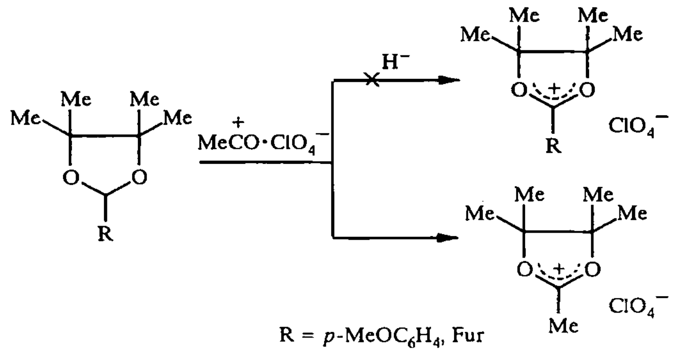
Salts of 1,3-dioxanium can be simply prepared by acylation of 1,3-dioxanes by carboxylic acid anhydrides in the presence of 70% $HClO_4$ [17, 18].



R^1 = Me, Fur, Ph, p-$MeOC_6H_4$; R^2 = H, Me; R^3 = H, Me; R^4 = Me, Et, n-Pr

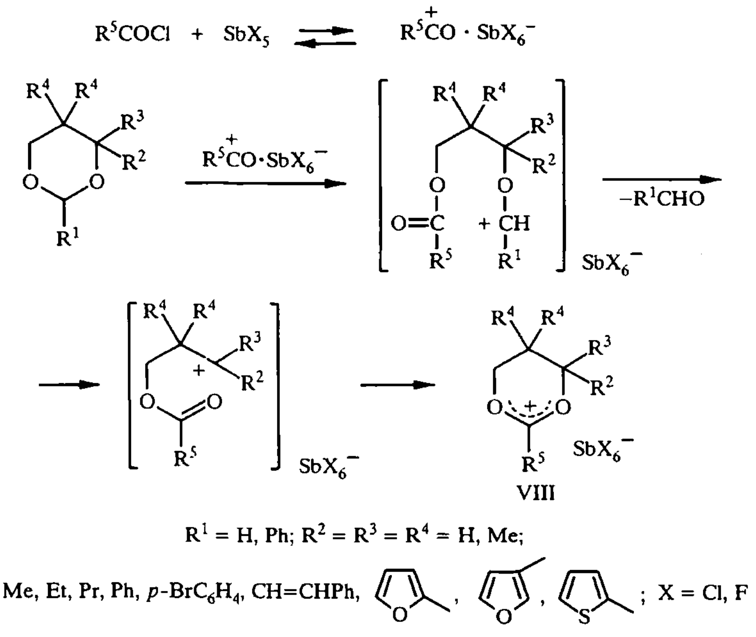
It was found that acylium perchlorate does not remove the hydride ion, but protonation and then acid-catalyzed opening of the 1,3-dioxane ring with subsequent formation of the intermediate cations A and B and cyclization of the latter into 1,3-dioxanium ion occur. The occurence of R^1CHO in the reaction mixture was proved by GLC.

It was also shown [19] that the proposed [20] removal of hydride ion from ring atom $C_{(2)}$ in the course the synthesis of 1,3-dioxolanium salts from 2-aryl- or furyl-substituted 4,4,5,5-tetramethyl-1,3-dioxolanes by reaction with acetyl perchlorate does not occur; 2,4,4,5,5-pentylmethyl-1,3-dioxolanium perchlorate are formed.



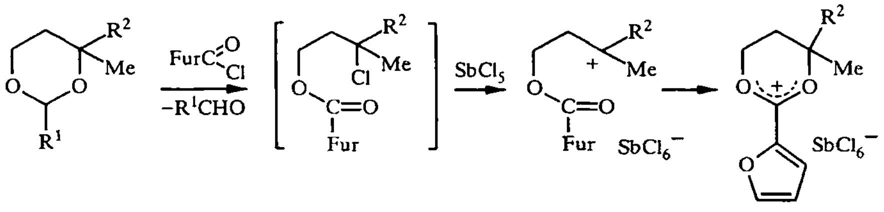
Perchlorates of 1,3-dioxanium substituted at 2-position in the ring can be easily prepared if industrial fractions of 4,4-dimethyl- and 4,4,5-trimethyl-1,3-dioxanes are used in this reaction [18].

The corresponding 2-alkyl-, 2-aryl-, and 2-hetaryl-substituted 1,3-dioxanium salts are obtained by acylation of 1,3-dioxanes with halides of aliphatic, benzoic, and furan(thiophene) carboxylic acids [21-28].

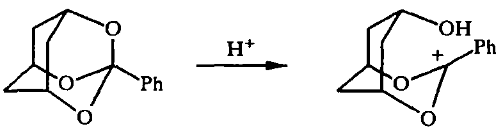


1,3-Dioxanium salts VIIIa-d [R^5 = Ph; $R^2 = R^3 = R^4$ = H (a); R^2 = Me, $R^3 = R^4$ = H (b); $R^2 = R^3$ = Me, R^4 = H (c); R^4 = Me, $R^2 = R^3$ = H (d)] have been prepared from benzoates of chlorohydrins [21].

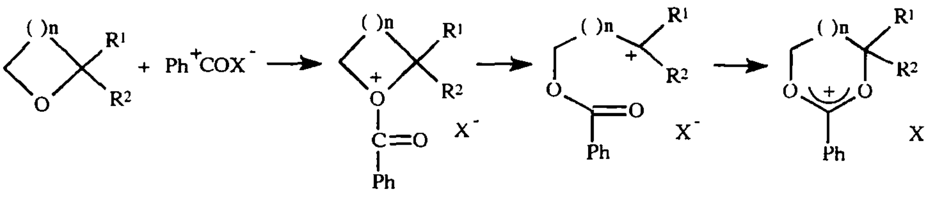
2-Furyl-substituted salts are obtained if the order of mixing the reagents is changed [21, 26, 28]. $SbCl_5$ as complexing reagent is added after chlorohydrin furoate has formed [11, 29, 30].



An acyloxonium ion was identified by UV and NMR spectra in solution of 3-phenyl-2,4,10-trioxaadamantane in sulfuric acid [31].



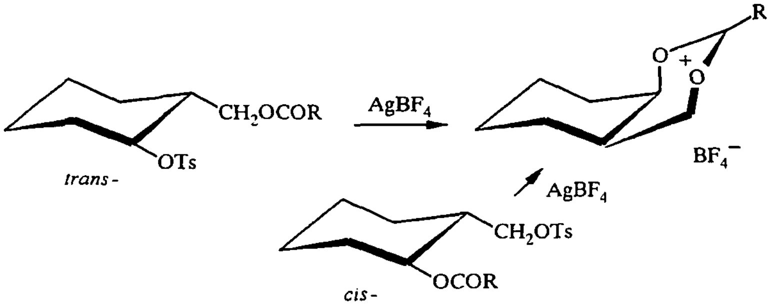
From cyclic ethers. Oxiranes and oxetanes in the presence of complexes $RC^{+}O{\cdot}X^{-}$ produce oxonium ion A [7], which isomerize into cation B – precursor of acyloxonium ions of 1,3-dioxolanium IX and 1,3-dioxanium VIII.



A B VIII a,b, IX a

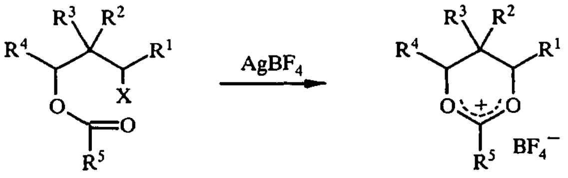
n = 0,1; X = $SbCl_6$; R^1 = H, Me; R^2 = Me, CH_2Cl

Cyclization of γ-substituted esters. Schneider and Kovacs first proposed cyclization of γ-tosylhydroxy(brosyl)-substituted esters of cyclohexanol as a method for preparing 2-methyl and 2-phenyl-1,3-dioxanium salts [10, 12, 32].



R = Me, Ph

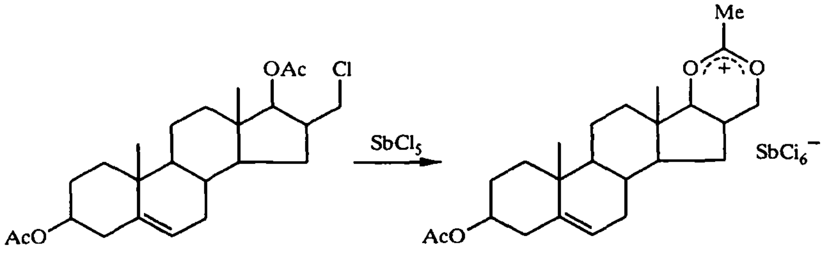
Acylates of γ-halopropanols are also converted by $AgBF_4$ into 1,3-dioxanium salts [11]. The yields of salts X were best for $R^2 = R^3 = H$.



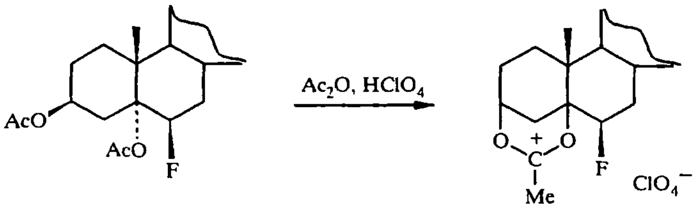
X

X = Cl, Br; $R^1 = R^2 = R^3 = R^4$ = H, Me, Et, Pr, Bu; R^5 = Me, Ph

This method was later used to prepare stable steroid cations [13].

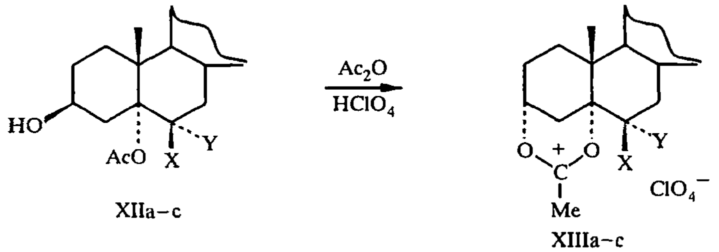


Stable 1,3-dioxanium steroid salts XI were prepared as perchlorates by reaction of 5α-5β-diacetoxy-6β-fluorocholestane with perchloric acid in acetic anhydride [33].



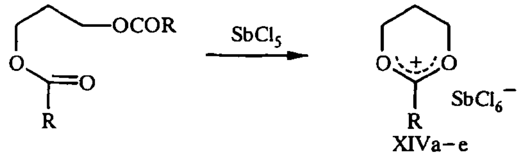
XI

Analogously ions XIIIa-c are obtained from 5α-acetoxy-3β-hydroxy derivatives of steroids XIIa-c [34]. These were earlier proposed as intermediates in the course of acylation of a series of chlorocholestanes [35-38].



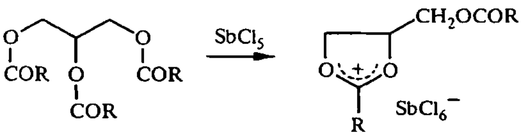
a X = Cl, Y = H; b X = OAc, Y = H; c X + Y = O

The 1,3-dioxanium salts XIVa-e were prepared by a simpler method through the reaction of esters of 1,3-diols with $SbCl_5$ [39]. Then the relative activity of neighboring groups and the influence of the size of the ring formed were studied [39-44].

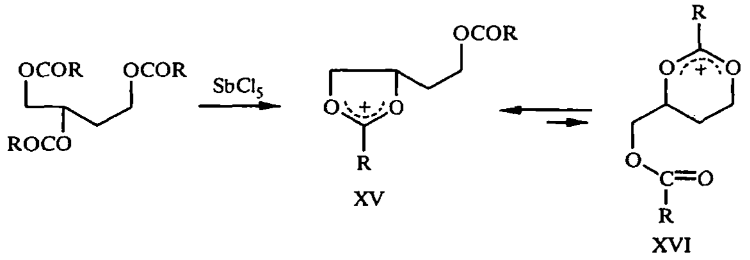


R = Me, *t*-Bu, Ph, *p*-MeC_6H_4, *p*-$MeOC_6H_4$

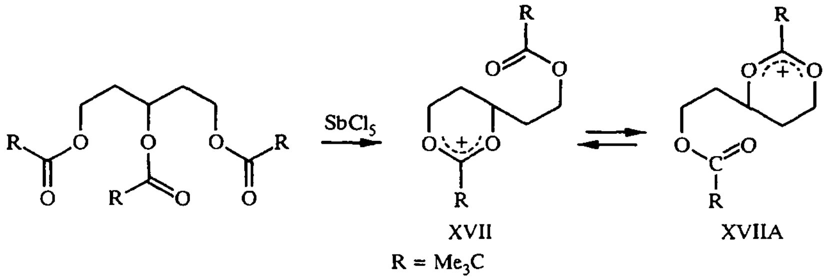
Cations of 1,3-dioxolanium and 1,3-dioxanium that are formed from esters of polyols exist in thermodynamic equilibrium. Only salts of 1,3-dioxolanium are obtained from esters of glycerol due to their higher thermodynamic stability in comparison with salts of 1,3-dioxanium [43].



Study of the reaction of 1,2,4-butanetriol ester with $SbCl_5$ made it possible to compare directly the stability of these cations. According to NMR data, the main product is salt XV with a five-membered ring. This is indicative of its higher stability when compared with the six-membered ring. However, equilibrium is possible. Nevertheless, the content of 1,3-dioxanium salts XVI in the mixture is very small [39].

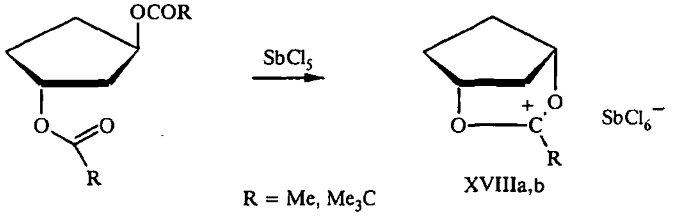


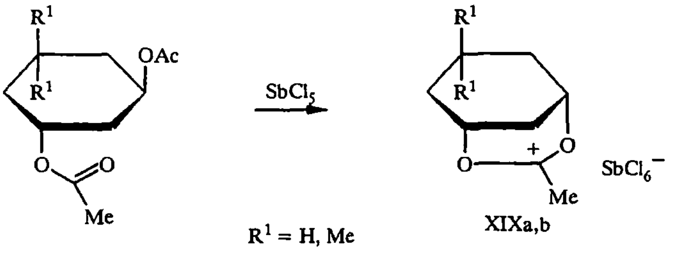
The reaction of 1,3,5-pentanetriol ester with $SbCl_5$ produces dioxanium ion XVII [40-42].



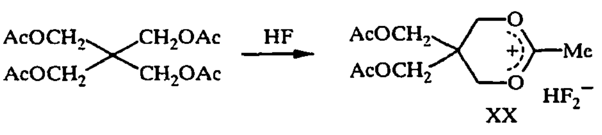
Cation XVII undergoes conversion to XVIIA, which has the identical structure. This was confirmed by NMR spectroscopy [39].

A characteristic feature of the reaction of cyclic esters of 1,3-diols with $SbCl_5$ is that only the *trans*-isomers react to form the corresponding *cis*-1,3-dioxanium salts. Thus, esters of *trans*-cyclopentane-1,3-diol and *trans*-cyclohexane-1,3-diol react with $SbCl_5$ to give 1,3-dioxanium salts XVIII and XIX, respectively [39]. The latter are formed faster than the former. This is explained by the strain of the five-membered ring in XVIII. Moreover, the equatorial and axial location of substituent along with the rapid inversion of ring in 1,3-diacetoxycyclohexane is favorable for reaction of the neighbouring group. The *cis*-isomers do not give the corresponding 1,3-dioxanium salts XIX and XVIII.

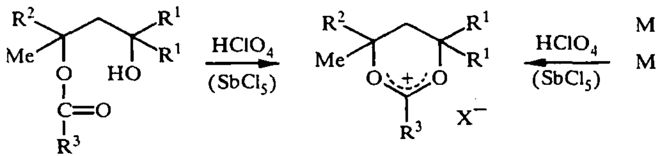




Paulsen *et al.* [39] report that 1,3-dioxanium salts XX are formed upon dissolution of pentaerythritol tetraacetate in liquid HF. NMR spectroscopy did not reveal the formation of bisacetoxonium ion pocessing the spiro configuration [39].

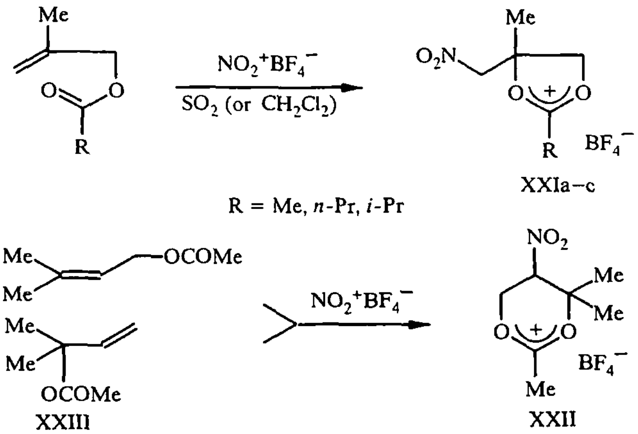


Salts of 1,3-dioxanium can be synthesized in quantitative yield from mono- and diesters of primary-secondary, secondary-tertiary and ditertiary 1,3-diols in the presence of $HClO_4$ or $SbCl_5$ [45-47].



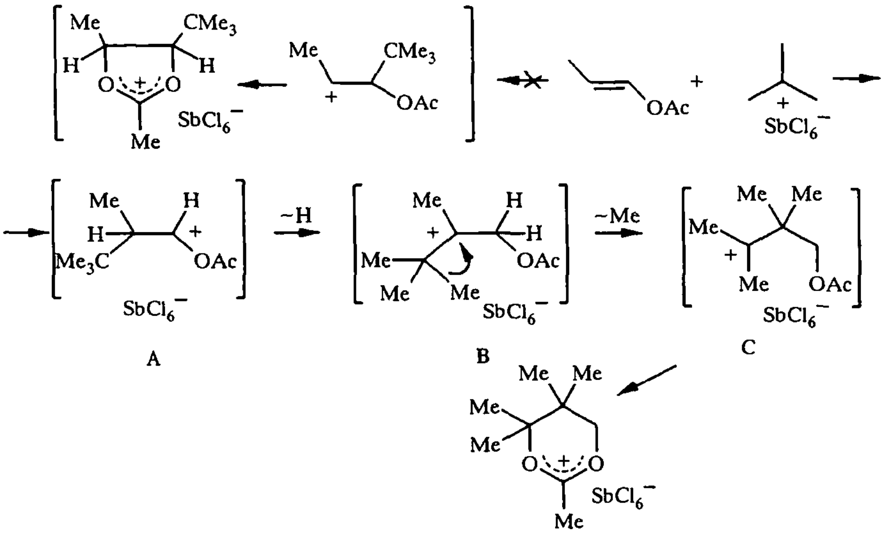
$R^1 = R^2 = H, Me; R^3 = Me, Ph; X = ClO_4, SbCl_6$

Nitration of allyl esters by NO_2BF_4 involves electrophilic attack of NO_2^+ on the C=C bond with nucleophilic participation of the neighboring carbonyl group. This leads to formation of NO_2-substituted acyloxonium salts, i.e., tetrafluoroborates of 2-alkyl-4-methyl-4-nitromethyl-1,3-dioxolanium XXIa-c and 2,4,4-trimethyl-5-nitro-1,3-dioxanium XXII [48].



R = Me, *n*-Pr, *i*-Pr

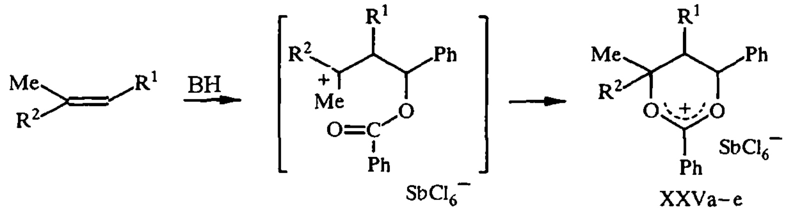
The salt XXII was prepared not only from γ-methyl crotyl acetate but also from dimethyl vinyl carbinol acetate XXIII and NO_2BF_4. In the latter case, anti-Markownikoff addition of NO_2^+ was observed [48]. Mursakulov *et al.* [48] proposed that analogous reactions that utilize other cationic electrophiles might provide access to other functionally substituted acyloxonium salts. The results of Dorofeenko and Luk'yanov are consistent with this [49-51]. Salt XXIV is obtained by alkylation of enol acetate of propionic aldehyde with trimethylcarbenium hexachloroantimonate. The reaction involves successive migration of H and the methyl group [49].



XXIV

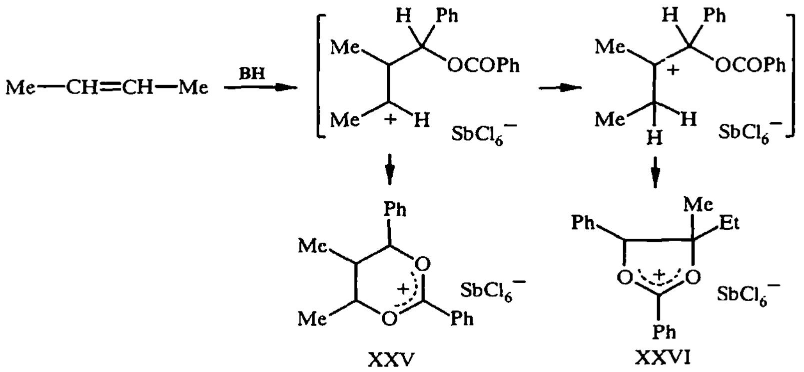
The authors propose the kinetically independent existence of the tertiary β-acyloxycarbocation B because the second migration obviously occurs instead of the fast cyclization. The acyloxy group destabilizes the β-carbenium center also: causing the methyl group to migrate with conversion from tertiary B to tertiary cation C. In other words, the neighbouring acyloxy group cannot affect the migrating group by a "push-pull" mechanism, i.e., rearrangement and cyclization are not coordinated.

The reaction of α-benzoyloxybenzylium hexachloroantimonate (BH) with unsaturated hydrocarbons enables 1,3-dioxanium salts with various substituents in the hydrocarbon part of the ring to be prepared [50, 51]. Using trialkylethylenes in the BH reaction yields a tertiary cation that gives stable 1,3-dioxanium hexachloroantimonates XXV upon cyclization.

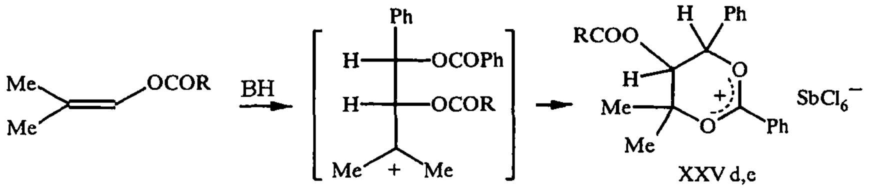


R^1 = H, Me, $OCOR^3$; R^2 = H, Me; R^3 = Me, Ph

Reaction of 2-butene (a mixture of *cis*- and *trans*-isomers) and BH gives a mixture of salts of 1,3-dioxanium XXV and 1,3-dioxolanium XXVI.

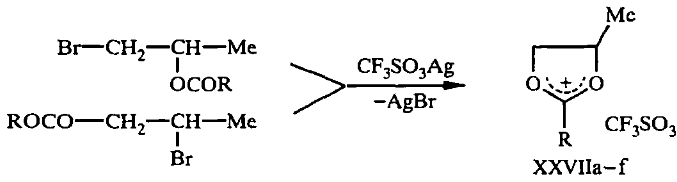


The secondary cation isomerizes into a tertiary one in the course of this reaction. However, direct cyclization of the former into salt XXV predominates. Salts XXV and XXVI were separated and determined to be present in an 8:1 ratio. If enol acylates are used as the unsaturated substrates, the resulting cation can cyclize through one of two ester groups (RCOO groups) to give 1,3-dioxolanium and 1,3-dioxanium salts. However, only the latter are isolated. The enol acetate forms a mixture of diastereomers XXVd that can be separated. However, enol benzoate gives only one isomer XXVe (R = Ph) [51].



R = Me, Ph

The synthesis of acyloxonium cations stabilized by trifluoromethanesulfonate anion $CF_3SO_3^-$ (triflate) from esters of 1-bromopropan-2-ol and 2-bromopropan-1-ol in the presence of silver triflate was proposed using 1,3-dioxolanium salts XXVII as an example [52].

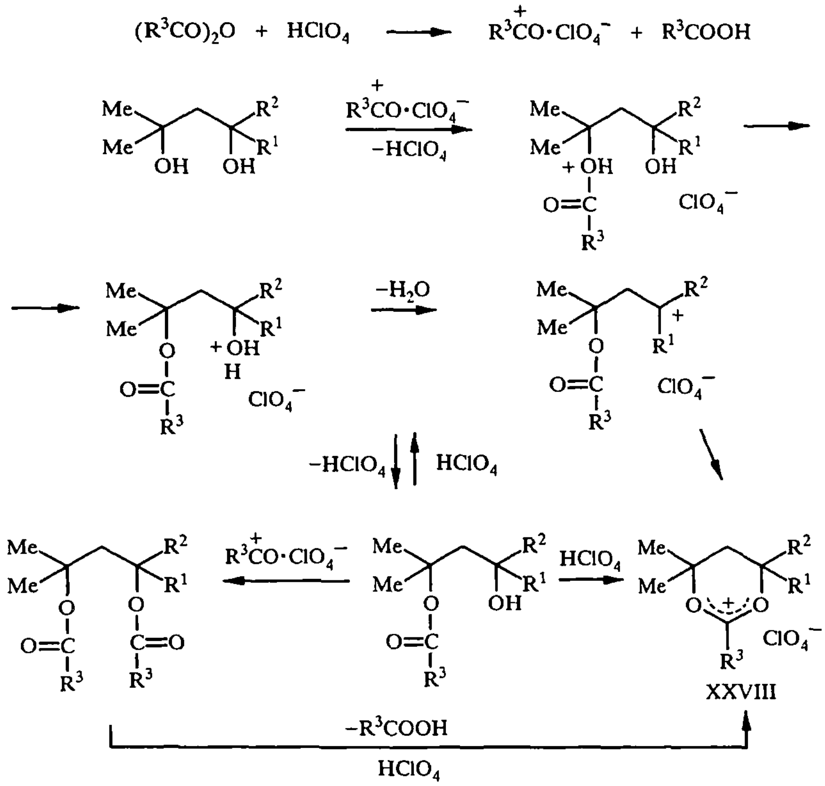


XXVIIa-f

R = Me, *i*-Pr, *t*-Bu, Ph, *p*-MeC_6H_4, *p*-$O_2NC_6H_4$

The stability of cations XXVII was demonstrated to depend on the nature of the R substituent in the 2-position. The stabilizing effect falls in the order *t*-Bu > *i*-Pr > Me > Ph > *p*-MeC_6H_4 > *p*-$O_2NC_6H_4$.

From 1,3-diols. The direct synthesis of 2-alkyl-1,3-dioxanium salts XXVIII by acylation of 1,3-diols with anhydrides of aliphatic acids in the presence of 70% $HClO_4$ is a preparatively simple method [47, 53-56].

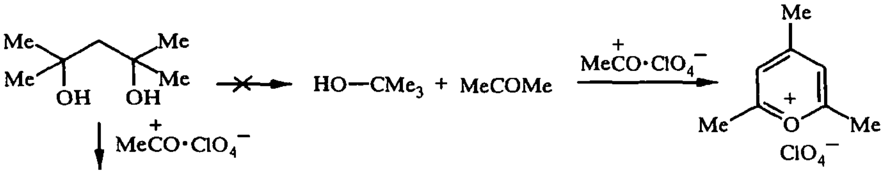


$$(R^3CO)_2O + HClO_4 \longrightarrow R^3\overset{+}{C}O\cdot ClO_4^- + R^3COOH$$

XXVIII

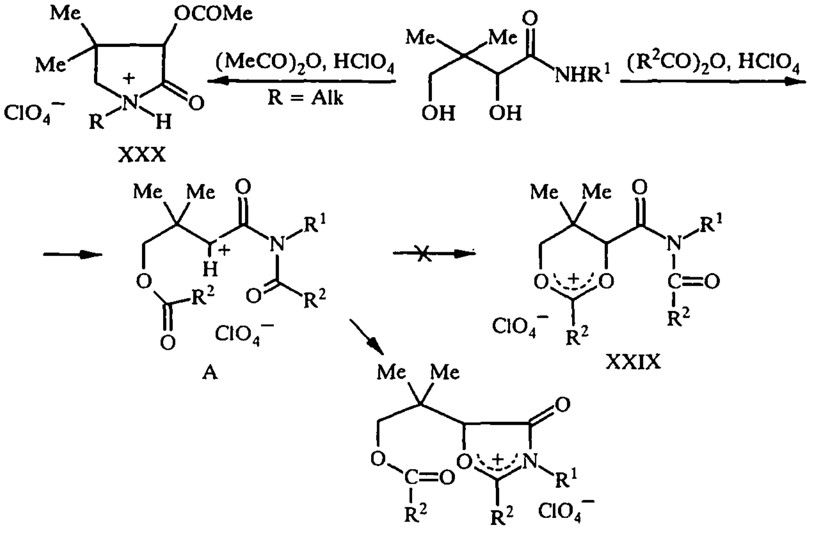
R^1 = H, Me; R^2 = H, Me, Et, Pr, Ph; R^3 = Me, Et, Pr

An alternative reaction route is known for acylation of pinacone, i.e., acid cleavage to the ketone and tertiary alcohol [56]. The latter reacts with acetyl perchlorate at elevated temperature to give pyrylium salts [57, 58]. However, only the 1,3-dioxanium salt XXVIII (R^1 = R^2 = R^3 = Me) is obtained at low temperature [47].



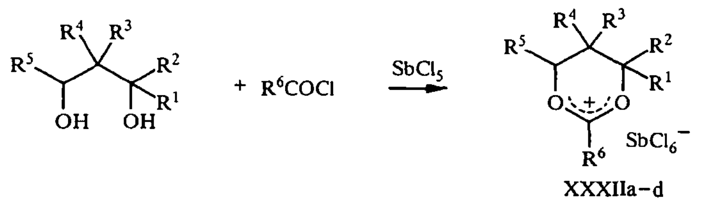
XXVIII

Using amides of 2,4-dihydroxy-3,3-dimethylbutanoic acid in this reaction does not yield 1,3-dioxanium salts XXIX. N-Substituted amides, retaining the characteristic tendency of γ-hydroxyamides to form heterocycles, give pyrrolidonium salts XXX. The products of O- and N-acylation cyclize through the ambident ion A to form the thermodynamically more stable five-membered cyclic 4(5H)-oxazolonium ion XXXI and not the six-membered cyclic acyloxonium ion XXIX [59, 60].

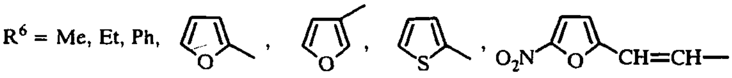


R^1 = H, Me; R^2 = Me, Et, Pr

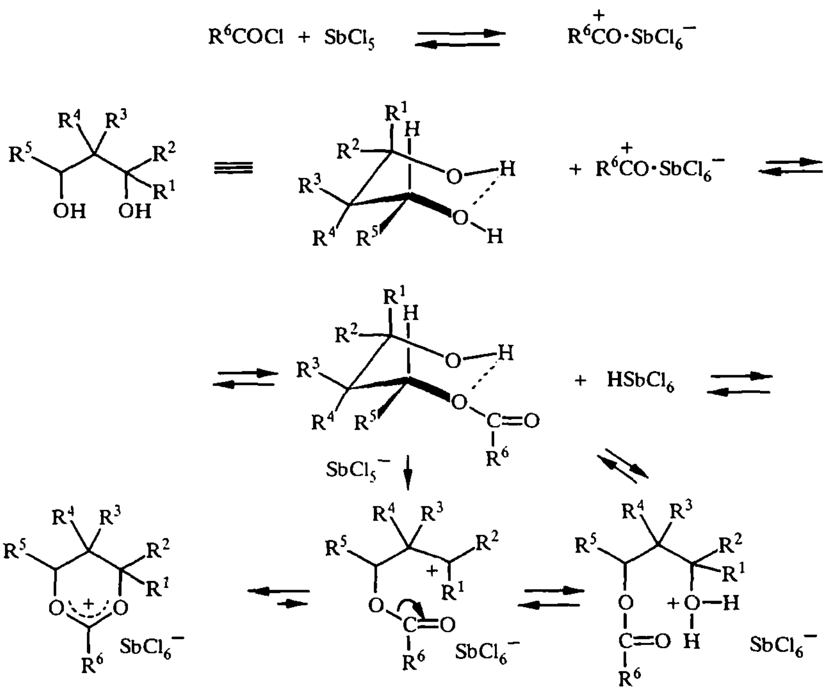
Acylation of 1,3-diols by acid chlorides in the presence of $SbCl_5$ produces 1,3-dioxanium hexachloroantimonates XXXII [26, 28, 46, 61-63].



$R^1 = R^2 = R^3 = R^4 = R^5$ = H, Me; R^1 = Pr, R^2, R^3 = $(CH_2)_3$, $(CH_2)_4$;

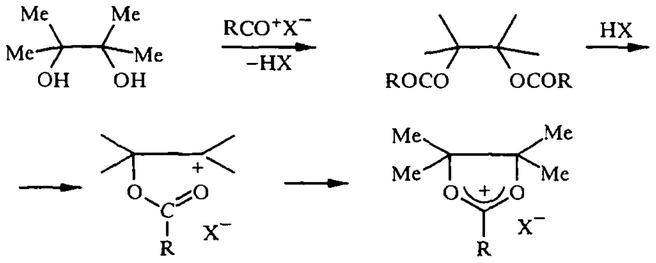


Primary-secondary, primary-tertiary and secondary-tertiary 1,3-diols can form 1,3-dioxanium salts [46, 62]. The primary hydroxyl group is evidently esterified in the first step of the reaction of acylium hexachloroantimonate with 1,3-diol. This is consistent with the known data that OH-group is preferentially acylated [64]. Water molecule is lost from cation A in acidic medium to form carbenium ion B, which cyclizes through intramolecular attack of the cationic center on the carbonyl oxygen of the ester group in XXXII. It has been proposed that the more stable the cation B, the easier it is formed and the higher is the cyclization rate. This was confirmed by experiment. Salt production is faster if donor substituents are added to the carbon atom carrying the positive charge.



XXXII B A

From pinacone 1,3-dioxolanium salts XXXIII are produced if acid chlorides and $AgClO_4$ (or $BF_3{\cdot}Et_2O$) are used [65].

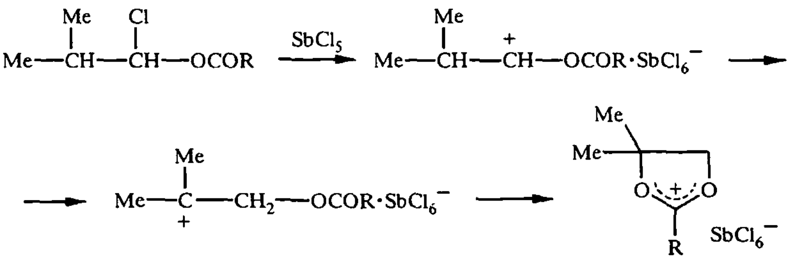


XXXIII

R = Me, Et, Pr, Ph, p-MeC_6H_4, p-BrC_6H_4, p-$MeOC_6H_4$, $PhCH_2$, $C_{10}H_7CH_2$, 3,4-$(MeO)_2C_6H_3CH_2$; X = ClO_4, BF_4

Paulsen and Schuttpelz [66] prepared a series of new derivatives of 1,3-dioxanium and 1,3-dioxolanium cations stabilized by ClO_4^- and BF_4^- anions. The syntheses were carried out as proposed by Meerwein [9] and Dorofeenko [1].

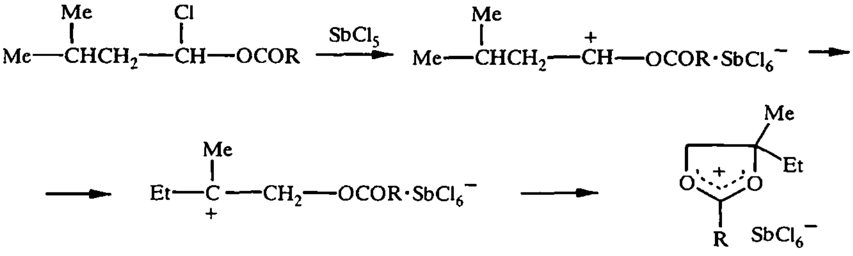
Reaction of $SbCl_5$ with solutions of α-chloroisobutyl acylates in CH_2Cl_2 produces 1,3-dioxolanium hexachloroantimonates XXXIV [67].



R = Me, Et, Ph

XXXIV

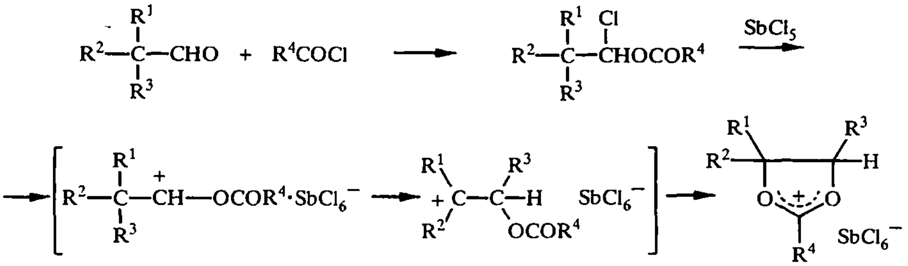
1-Chloro-3-methylbutyl acylates and $SbCl_5$ yield 4-methyl-4-ethyl-2-R-1,3-dioxolanium salts XXXV and unexpected 2-R-4,4-dimethyl-1,3-dioxanium hexachloroantimonates. This is explained by rearrangement of the intermediate acyloxycarbocation [68].



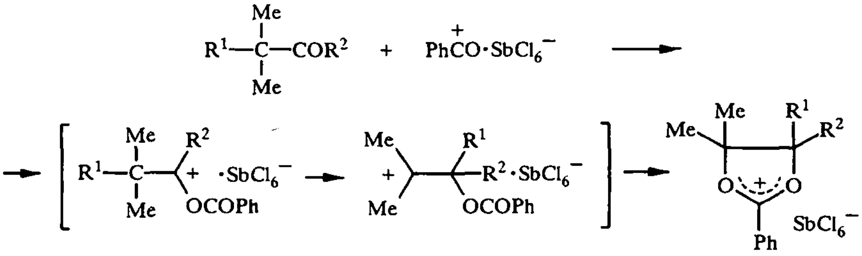
R = Me, Ph

XXXV

1,3-Dioxolanium salts can be prepared from 2-chloroacylates without isolating the latter during acylation of α-branched aldehydes [69].



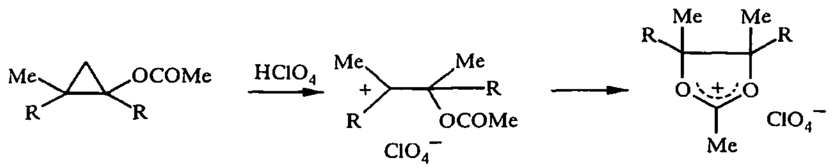
Dorofeenko and Luk'yanov performed a series of syntheses of 1,3-dioxolanium salts XXXVI using the ability of carbonyl compounds to be acylated [67-71]. The carbonyl compounds form acyloxycarbocations in the presence of $SbCl_5$. These can rearrange into 1,3-dioxolanium salts [70].



XXXVI

$R^1 = R^2 = H, Me; R^1 = CH_2Ph$

The ability in principle to synthesize 1,3-dioxolanium salts XXXVII from esters of cyclopropanols was also demonstrated [68].



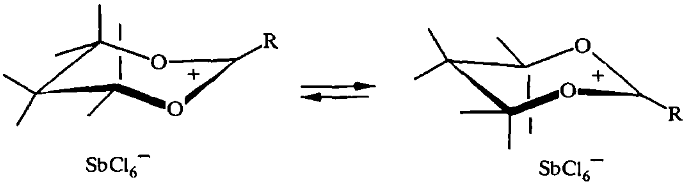
XXXVII

R = Me, Et, Pr

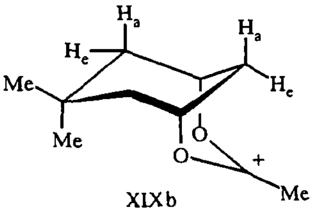
SPECTRAL CHARACTERISTICS OF 1,3-DIOXANIUM SALTS

The most informative spectral methods for establishing the structure of 1,3-dioxanium salts are ^{1}H and ^{13}C NMR spectroscopy [2, 15, 17, 21, 26, 39, 47-51, 55, 62, 63, 66].

NMR spectra of the salts are reviewed by Paulsen and Behre [2]. For 1,3-dioxanium salts, like for those of 1,3-dioxolanium, the proton signals of the substituent on the *meso* carbon $C_{(2)}$ that appear as a singlet with chemical shift (CS) $\delta = 2.57\text{-}2.85$ ppm and of the protons on $C_{(4)}$ and $C_{(6)}$ with $\delta = 4.95\text{-}5.97$ ppm are strongly shifted to weak field owing to the positive charge. The spin-spin coupling constants (SSCCs) $^{3}J_{45} = {}^{3}J_{56} = 5.6$ Hz suggest that the six-membered ring adopts the chair conformation and is fluxional [39].

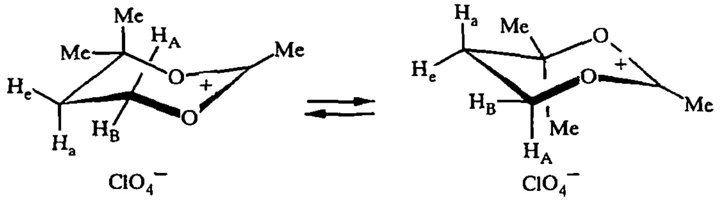


The conformation of the dioxanium ring in the bicyclic compound XIXb is tentatively assigned judging from the fact that the cyclohexane ring exists in the chair conformation with the diaxial location of oxygen atoms of the carboxonium bridge [39].



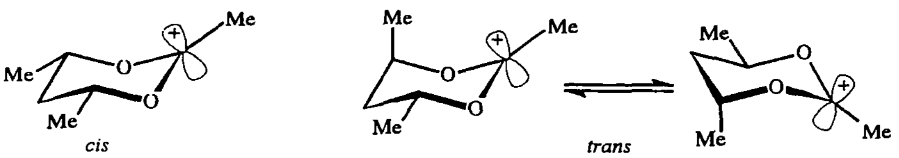
XIXb

The nature of the splitting of the resonance signals for 2,4,4-trimethyl-1,3-dioxanium perchlorate suggested [17] that the six-membered heterocyclic ring interconverts at a rate that is rapid on the NMR time scale either chair – chair or within a family of flexible conformations. The protons of the *gem*-dimethyl group resonate as a singlet whereas those at $C_{(5)}$ and $C_{(6)}$ appear as triplets with $\delta = 2.54$ and 4.97 ppm and SSCC $^{3}J_{56} = 6.0$ Hz. Interconversion of the ring was observed even at -90°C.



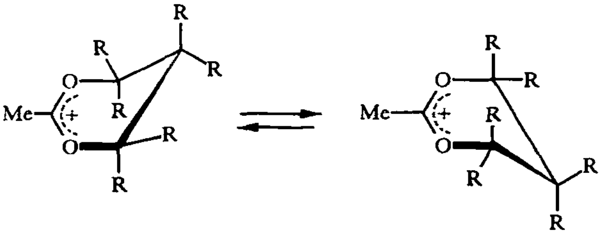
The weak-field proton shift $\Delta\delta = \delta$ dioxane - δ cation for the 5-CH_2 and 6-CH_2 groups of 2,4,4-trimethyl-1,3-dioxane and the corresponding salt ($\Delta\delta = -1.34$ and -1.38 ppm, respectively) has been determined, when the molecules of both compounds undergo rapid conformational isomerization. The $\Delta\delta$ values are rather large. A comparison of the calculated $\Delta\sigma$ and $\Delta\delta$ indicates that the experimental and calculated $\Delta\sigma$ for the 6-CH_2 protons agree satisfactorily for the approximation used. The nature of weak-field shifts $\Delta\delta$ of the methylene protons is generally attributed to the effect of the electric field formed by the positive charge on $C_{(2)}$ [17].

Significant shifts to weak field are observed for signals from the protons of the methyl groups and those at the 2-, 4- and 6-positions on the ring in 2,4,6-trimethyl-1,3-dioxanium cations in the *cis*- and *trans*-conformations [15].

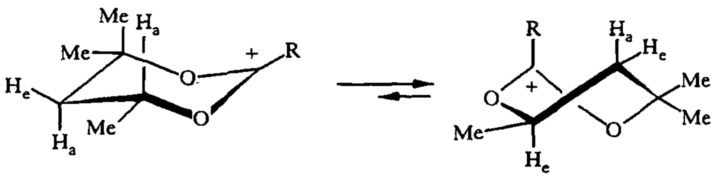


Paulsen *et al.* investigated the ^{1}H and ^{13}C NMR spectra of a series of 1,3-dioxanium salts substituted at $C_{(2)}$, $C_{(4)}$, $C_{(5)}$ and $C_{(6)}$. Linear correlations exist between the ^{13}C CSs of $C_{(2)}$ and the magnitude of the π-charge calculated by MINDO/3. The anisotropy of the magnetic shielding caused by mesomeric effects of the cationic system explains the NMR shift of the protons in the α-position of the substituent at $C_{(2)}$ of the cation [66].

Regardless of the previously established chair conformation for the six-membered acyloxonium cation [39], MINDO/3 quantum chemical calculations [66] and X-ray structural data [73] for 1,3-dioxolanium salts indicated a planar disposition for the five atoms $C_{(6)}$–$O_{(1)}$–$C_{(2)}$–$O_{(3)}$–$C_{(4)}$ of the six-membered ring. The vicinal SSCCs between the protons at $C_{(4)}$ (or $C_{(6)}$) and $C_{(5)}$ $^3J_{56} = {}^3J_{54} = 5.6$ Hz are consistent with envelope – envelope conversion for R = H. A preference for the envelope conformation with the substituents in the equatorial positions is proposed for cations substituted at $C_{(4)}$, $C_{(5)}$, and $C_{(6)}$.

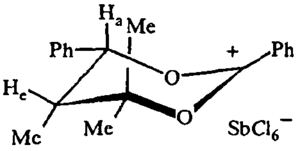


Another viewpoint regarding the conformation of the six-membered ring has been expressed because the X-ray structural data relate to the crystalline state whereas the conformation in solution may differ [62]. The 1,4-*twist* conformation has been demonstrated to dominate for 2,4,4,6-tetramethyl- and 2-phenyl-4,4,6-trimethyl-1,3-dioxanium salts. The vicinal SSCCs $^3J_{Aa} = 116$ Hz and $^3J_{Ae} = 3.5$ Hz support this.

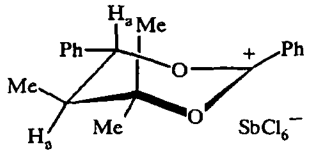


R = Me, Ph

According to PMR spectral data, 4,4,5-trimethyl-2,6-diphenyl-1,3-dioxanium hexachloroantimonate is obtained as two diastereomers represented as rings in the chair conformation with axial-equatorial and diaxial $H_{(4)}$ and $H_{(5)}$ [51].



$^3J_{ae} = 11$ Hz



$^3J_{ae} = 2{,}0$ Hz

However, the NMR spectra suggest not only that the structure and stereochemistry of the six-membered heterocyclic cation are correct but also that the substituents affect the stability of the salts in proportion to the CS of the protons in the 1,3-dioxanium ring.

Substituents at $C_{(2)}$ of the extended $O–C^+–O$ fragment affect mostly the weak-field CSs of $H_{(4)}$ and $H_{(6)}$. They fall into a series according to the weakening effect on the delocalization of the positive charge. The magnitude of the CSs of $H_{(6)}$ for 4,4-dimethyl-1,3-dioxanium salts is rather large, $\Delta\delta = -0.56$ ppm [21, 26, 62, 63], if the R group in the 2-position changes from Me to Ph:

Me > Pr > Et > 5-NO_2FurCH=CH > 2-Fur > Ph

According to the literature [39, 66], a series of substituents that affect the delocalization of the positive charge in 2-substituted 1,3-dioxanium salts can be arranged in the following order ($\Delta\delta = \delta_{Me} - \delta_{FPh} = 4.92 - 5.12 = -0.2$ ppm):

Me > Et > Pr > *t*-Bu > *i*-Pr > *n*-Bu > Ph > 4-FC_6H_4.

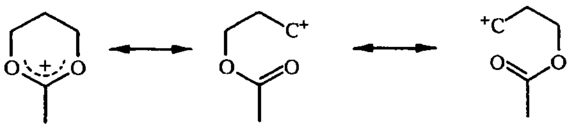
IR spectra of 1,3-dioxanium salts have been studied only for a few representatives owing to their hygroscopicity [17, 21, 26, 47, 63]. Like as for their five-membered structural analog 1,3-dioxolanium, 2-alkyl substituted 1,3-dioxanium cations exhibit two intense absorption bands at 1585-1540 and 1525-1490 cm^{-1}. These bands are assigned to vibrations of the $O–C^+–O$ fragment. The significant shift to higher frequencies for the bands of the mesomeric moiety, when compared with those for 1,3-dioxolanium salts, indicates that the positive charge is less delocalized. A group of bands including those of C=C vibrations of the aromatic ring at 3080-3100, 1595-1580, 1550-1530, and 1520-1500 cm^{-1} is observed if Ph and Fur substituents are present at $C_{(2)}$ [26, 50].

The peak with $\lambda_{max} = 265$ nm in UV spectra of 2-phenyl-1,3-dioxanium salt is characteristic of similar ions [$PhC^+(OMe)_2$, 2-phenyl-1,3-dioxolanium cation] containing the $O–C^+–O$ fragment [1, 31].

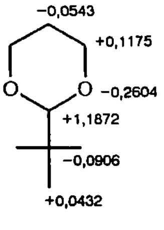
TRANSFORMATIONS OF 1,3-DIOXANIUM SALTS

Among cyclic acyloxonium cations, 1,3-dioxanium salts are less stable than 1,3-dioxolanium salts [39]. Their stability corresponds to the number, location and donor strength of the substituents. This can be explained by both the steric hindrance to nucleophilic attack and the greater effective delocalization of the positive charge [47]. Calorimetry data and NMR spectra [74] demonstrated that 2-methyl substituted 1,3-dioxanium salts are anomalously, from the viewpoint of electronic effects, more stable than 2-phenyl derivatives and, therefore, they are less reactive.

Considering the reactivity of 1,3-dioxanium salts their ambident nature must be noted being evident in the reactions of nucleophilic reagents at $C_{(2)}$ and $C_{(4)}$ of the heterocycle. The dual reactivity of these compounds is a result of delocalization of the positive charge, which can be described by resonance structures [1, 2]:



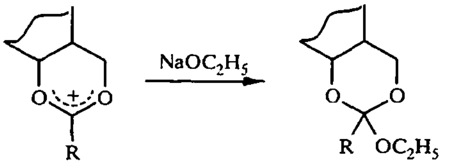
Meerwein [75] first observed the dual nature of the cyclic carboxonium ions. The nature of the final products is determined by the strength of the bond formed as result of the initial nucleophilic attack on the dioxanium cation and by the ability of the product formed to dissociate at this bond. Nucleophile is added most easily at the 2-position of the heterocycle, which has the smallest electron density according to quantum-chemical calculations [47, 66].



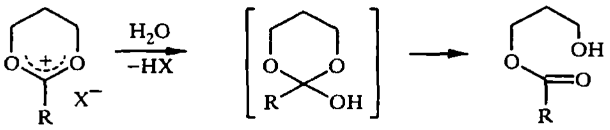
Moreover, the reaction direction depends on the energy of the cation itself, the nature of the nucleophile, the temperature, the reaction time and the solvent [2].

Recent results have demonstrated that 1,3-dioxanium cations are of interest as active synthetic reagents and are promising for practical use. The reactivity patterns of acyloxonium cations with nucleophilic reagents have been reviewed in detail for 1,3-dioxolanium [1, 2] and certain 1,3-dioxanium salts [2]. Reactions of 1,3-dioxanium salts that are known at this time are reviewed below.

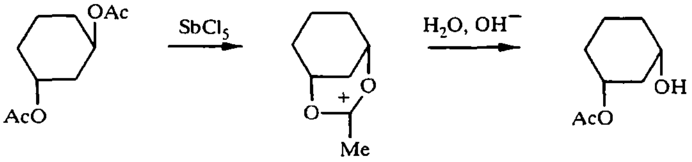
Nucleophilic addition at the 2-position of the 1,3-dioxanium ring. 4-Methyl- and 4,5-tetramethylene-1,3-dioxanium salts react readily at room temperature with sodium alcoholate to form the corresponding 2-alkoxy-1,3-dioxanes [11, 33, 75, 76].



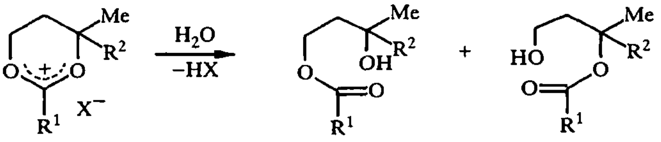
In all cases, addition of water is accompanied by proton-assisted opening of the heterocycle to produce monoesters of 1,3-diols, that are difficult to produce in a pure state by acylating the 1,3-diols [17, 21, 33, 34, 39, 46, 47, 51, 63].



This reaction is a convenient preparative method for converting esters of *trans*-glycols into the *cis*-isomers [39].

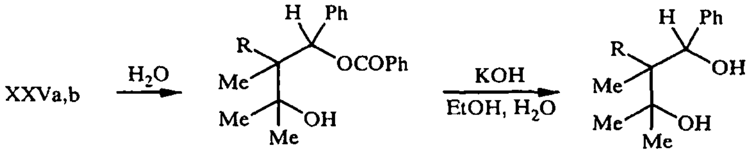


Asymmetric salts of 1,3-dioxanium hydrolyze to form structural isomers in a ratio that depends on the nature of R^1 [47, 63].



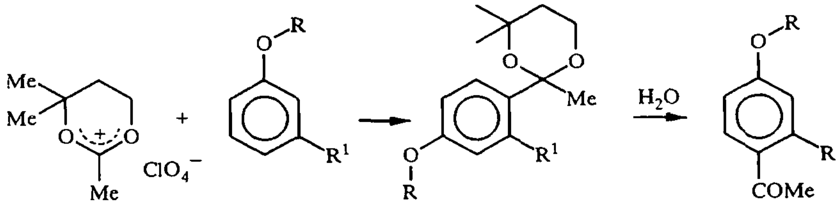
R^1, R^2= Ph, Fur, thienyl

Hydrolysis of 4,4,5,6-substituted salts of 1,3-dioxanium XXV, which are prepared from the α-chloroalkyl acylates, is a good method for preparing derivatives of 1,3-glycols, competing with the Prins reaction [77]. The isolated γ-hydroxy esters are easily hydrolyzed by an aqueous–ethanolic solution of KOH into 1,3-diols in 93-96% yield [51].



R = H, Me

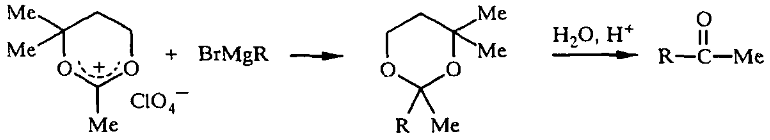
The reactions of 1,3-dioxanium salts with nucleophiles, the addition of which generates new C–C bonds, have been studied using electrophilic substitution on phenols and their ethers as examples [78].



R = H, Me; R^1 = H, OH, OMe

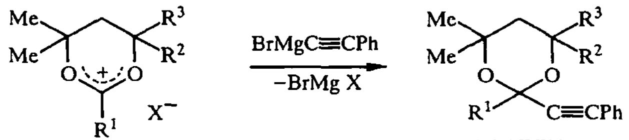
The resulting 2-aryl-substituted 1,3-dioxanes are not isolated but immediately subjected to acid hydrolysis to form aromatic ketones. Thus, reaction of 1,3-dioxanium salts with organic nucleophiles results in acylation of the latter. The yield of ketones is comparatively low. Their preparation is accompanied by the formation of resinous products, which is explained by ion-induced polymerization of the products [79].

Stable C–C bonds in 1,3-dioxanium salts are also formed in reactions with organometallic compounds; so a series of difficultly accessible 2,2-disubstituted 1,3-dioxanes are obtained. The reaction of 2,4,4-trimethyl-1,3-dioxanium perchlorate with Grignard reagent produces pure 2-methyl-2-alkyl-substituted 1,3-dioxanes in high yield [80].



R = Me, Et, *n*-Pr, *n*-Bu, Ph

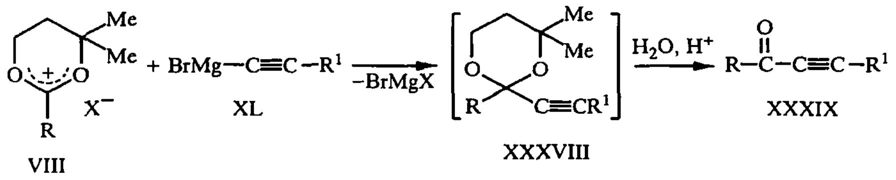
1,3-Dioxanium salts exhibit properties analogous to Iotsich reagents. They form the previously unknown 2-phenylethynyl-1,3-dioxanes XXXVIII upon mixing the reagents at room temperature [81].



XXXVIII

X = ClO_4, $SbCl_6$, R^1 = Me, Ph; R^2 = H, Me; R^3 = H, Me

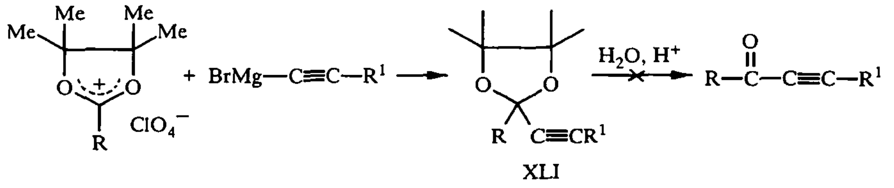
2,4,4-Trimethyl-2-R-ethynyl-1,3-dioxanes readily hydrolyze to α-acetylenic ketones XXXIX in yields of 42.0-84.4%. The same products result from type VIII 1,3-dioxanium salts and Iotsich reagents XL without isolation of the intermediate 1,3-dioxanes. The reaction mixture is decomposed with 10% HCl [82].



R = Me, Ph, Fur; R^1 = CH_2OH, Ph

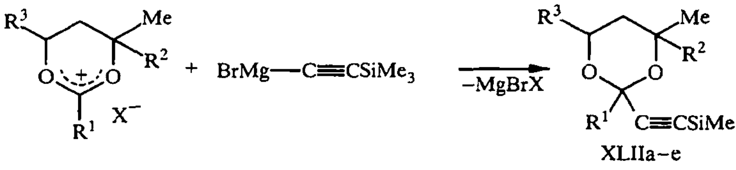
The preparation of α-acetylenic ketones by a one-step synthesis enables furoylacetylenes to be obtained by a simpler method than those known, which involve two steps [83].

Shchelkunov and Rofman [84] proposed the synthesis of 2-ethynyl-substituted 1,3-dioxolanes from 2,4,4,6,6-pentamethyl-1,3-dioxolanium perchlorate and Iotsich reagent. However, they were unsuccessful in preparing α-acetylenic ketones by hydrolysis of 1,3-dioxolanes. In weakly acidic medium, the hydrolysis is inhibited. Under more drastic conditions, the resinification of the starting 2-ethynyl-1,3-dioxolanes XLI occurs.



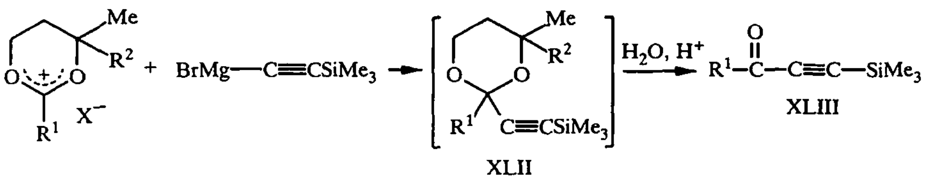
R = Alk; R^1 = $CH{=}CH_2$, Ph, CH_2OH, CMe_2OH, CMeEtOH, $CMeOCMe_2CMe_2O$

A series of silicon-containing 1,3-dioxanes XLII, which are difficultly accessible by other methods, was synthesized by reacting 1,3-dioxanium salts with trimethylsilylethynyl magnesium bromide [63, 85, 86].



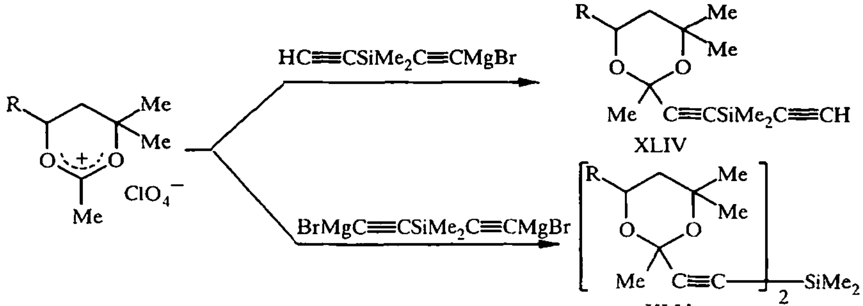
X = ClO_4, $SbCl_6$; R^1 = Me, thienyl, Ph; R^2 = H, Me; R^3 = H, Me

This reaction is important for synthesis of acetyl-, furoyl-, thenoyl-, and benzoyltrimethylsilylacetylenes XLIII, which are prepared in one step, 1,3-dioxanes XLII being hydrolyzed without isolating from the reaction mixture [85, 86].



R^1 = Me, Fur, thienyl, Ph

The reaction of Iotsich reagents obtained from dimethyldiethynylsilane and 2,4,4-trimethyl- and 2,4,4,6-tetramethyl-1,3-dioxanium perchlorates leads to 1,3-dioxanes XLIV and XLV processing one and two rings in the structures [55, 87].

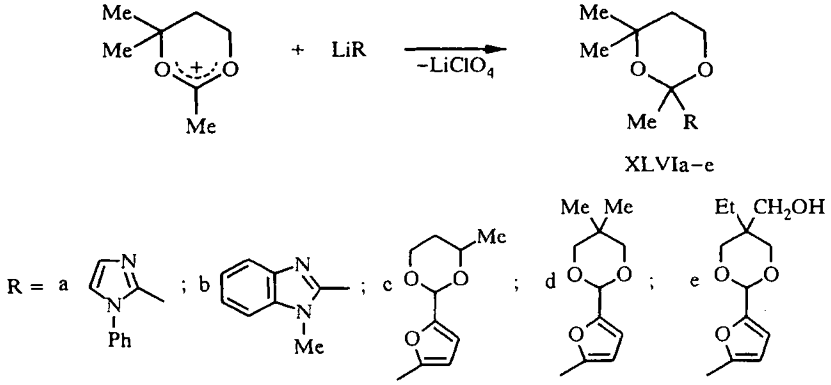


XLIV

XLV

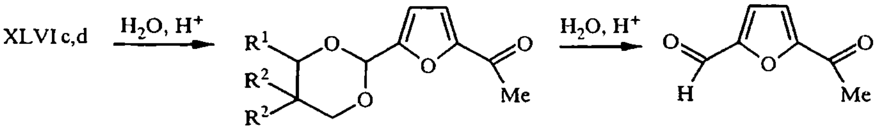
R = H, Me

The reaction of organolithium compounds with 2,4,4-trimethyl-1,3-dioxanium perchlorate yields 2-hetaryl-1,3-dioxanes XLVIa-e [80, 88].



XLVIa–e

In acidic medium 1,3-dioxanes XLVIa-d are hydrolyzed to the corresponding ketones. In weakly acidic medium bis-1,3-dioxanes XLVIc and d are hydrolyzed only at the ketal moiety to form the methyl ketones XLVIIa, b. This is consistent with a lower hydrolytic stability for the ketal ring compared with the acetal ring [80].

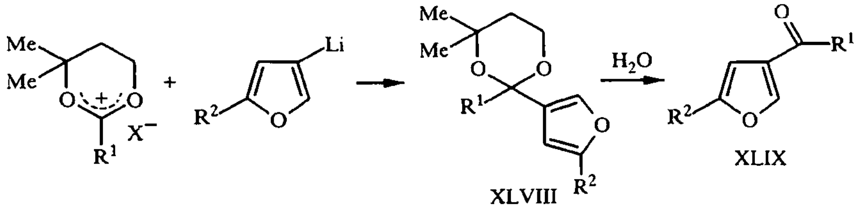


XLVIIa,b

a R^1 = Me, R^2 = H; b R^1 = H, R^2 = Me

The difficultly accessible 2-acetyl-N-phenylimidazole and 2-acetyl-N-methylbenzimidazole are obtained by carrying out this procedure without isolating the 1,3-dioxanes XLVIa and -b [80].

The reaction of 1,3-dioxanium salts with 3-Li-furans produces 2-(3-furyl)-1,3-dioxanes XLVIII, which are easily converted to β-acyl derivatives of furan XLIX [89].

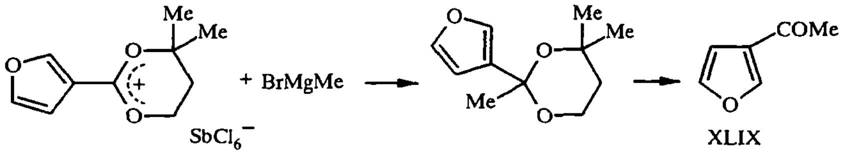


XLVIII

XLIX

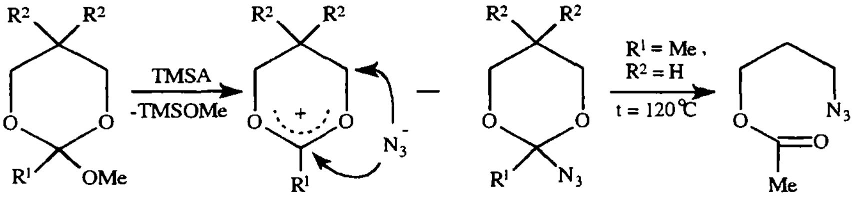
R^1 = Me, Ph; R^2 = H, Me

The ketone XLIX (R^1 = Me, R^2 = H) is prepared directly from 4,4-dimethyl-2-(furyl-3)-1,3-dioxanium hexachloroantimonate and methylmagnesium bromide [90].



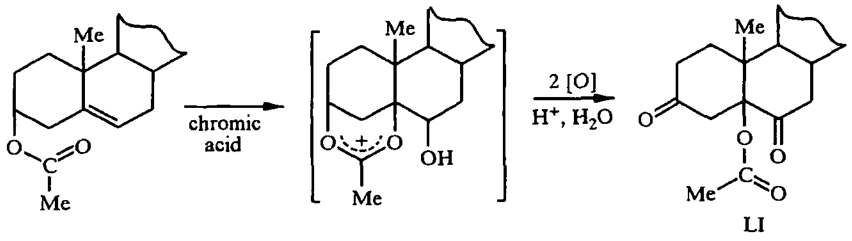
For example, using 2,4,4-trimethyl-1,3-dioxanium salt in the reaction with $LiAlH_4$ at room temperature in 15-20 min produces 1,3-dioxane L in high purity and high yield [80].

The cyclic orthoester of glycol reacts with trimethylsilyl azide by dissociation of the intermediate 1,3-dioxanium cation to produce 2-azido-2,5,5-trimethyl-1,3-dioxane. 1,3-Dioxane unsubstituted in the 5-position isomerizes into 3-azidoprop-1-yl acetate [91].

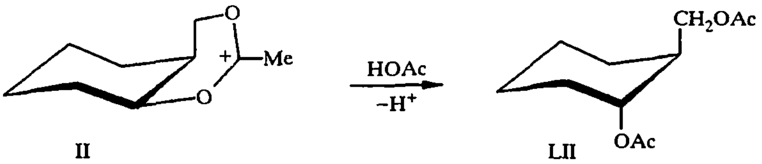


R^1 = Me, Ph; R^2 = H, Me

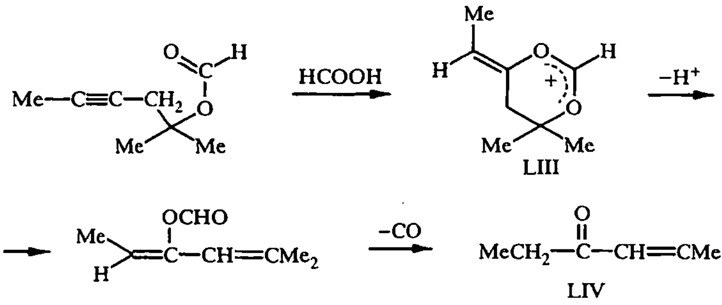
Reactions at the 4-position accompanied by dioxane ring opening. Oxidation of steroids by chromic acid with intermediate formation of a 1,3-dioxanium salt produces ketones LI [92].



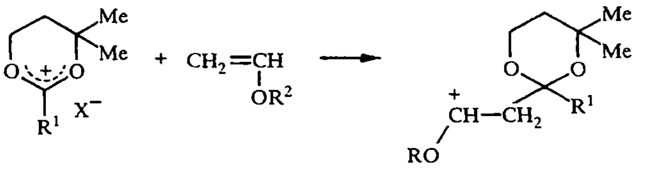
Diacetates of 1,3-glycols LII are obtained by attack of acetate anion on $C_{(4)}$ of the 1,3-dioxanium cation II [12, 77].



Addition of formic acid to the triple bond of 2-methyl-4-hexyne-2-ol formate gives the ketone LIV through the 1,3-dioxanium cation LIII [93].



According to the literature [94], 1,3-dioxanium salts can be used for initiation of cationic polymerization of vinyl ethers by forming the monomer to be polymerized.



R^1 = Me, Et, Pr, Ph; R^2 = Et, Bu; X = ClO_4, $SbCl_6$

4,4-Dimethyl-2-phenyl-1,3-dioxanium hexafluoroantimonate is recommended as a convenient industrial initiator for cationic oligomerization of α-oxides and other cyclic ethers.

Thus, 1,3-dioxanium salts are successfully used to synthesize a variety of substituted heterocyclic systems. Further research in this direction is an important and timely issue.

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