ION-RADICAL AND REDOX TRANSFORMATIONS OF CYCLIC ACETALS (REVIEW)

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A review of research dealing with ion-radical and redox transformations of cyclic acetals in the liquid phase is given.

Owing to their interesting physicochemical properties, high reactivities, and efficient practical utilization, cyclic acetals have been of constant interest to researchers. The problems involved in the synthesis and homo- and heterolytic reactions of compounds of this class have been illuminated in detail in a number of monographs and review publications [1-7]. Their radical-chain isomerization to the corresponding esters, which, in a number of cases, are difficult to obtain by different methods, have been found to be of value and interest for preparative chemistry. The homolytic halogenation and oxidation of cyclic acetals are of substantial value for organic sysnthesis. Diverse linear and cyclic dimeric and telomeric products that contain various functional groups can be obtained as a result of the radical addition of these compounds to carbon—carbon multiple bonds. Reviews [4-7] have been devoted to the analysis and systematization of these data. However, a number of studies that open up new synthetic possibilities associated with ion-radical and redox transformations of substituted 1,3-dioxacyclanes have been published in the last 5 yrs. In this connection, in the present review we have summarized the principal methods and results of reactions of this type in series of cyclic acetals.

Anion-Radical Transformations of Acetals

The possibility of the generation of anion radicals from acetals of nitroalkanols or nitrobenzaldehydes was demonstrated in [8, 9]. In the reaction of 2-nitrophenyl-1,3-diheterocycloalkanes I with the dipotassium salt of cyclooctatetraene in tetrahydrofuran (THF) at 20°C in an inert atmosphere, electron transfer from the cyclooctatetraene dianion to the nitro group occurs, as a result of which the corresponding anion radicals Ia are formed.

R = 1,3-dioxan-2-yl or substituted 1,3-dioxan-2-yl, 1,3-dioxazin-2-yl, 1,3-diisobutylimidazolidin-2-yl, 1,3-oxathiolan-2-yl, and 1,3-dithiolan-2-yl.

The latter are readily recorded in the EPR spectra and display sufficient stability in an inert atmosphere at -50°C to 40°C. In all cases the yield of cyclooctatetraene is close to quantitative, and this constitutes evidence for virtually complete conversion of starting I to anion radicals Ia. In [8, 9] the effect of the 1,3-diheterocycloalkyl substituent on the π-electron system of the aromatic ring was judged from EPR, PMR, and mass-spectral data. It was established that both in the base and the anion- and cation-radical states the introduction of a 1,3-diheterocycloalkyl substituent increases the hyperfine interaction (HFI) constants a_N, shifts the center of the multiplet of the aromatic ring protons to strong field, and increases the intensity of the molecular ion in the mass spectra, in much the same way as an amino group, in contrast to the acceptor effect of a nitro group, creates this effect.

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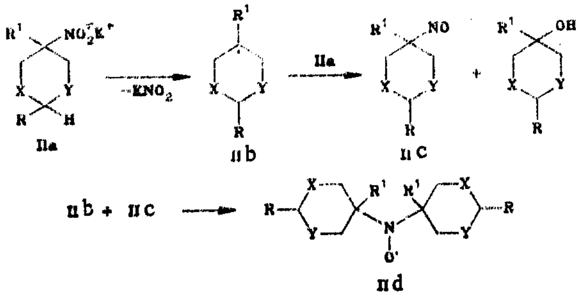
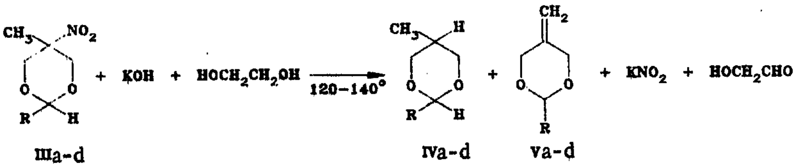
In contrast to aromatic substrates I, in the reaction of 5-alkyl-5-nitro-1,3-diheterocycloalkanes II with the dipotassium salt of cyclooctatetraene in THF one observes in the EPR spectra the presence of signals related to two paramagnetic particles: anion radicals of 5-alkyl-5-nitro-1,3-diheterocycloalkanes (a_N = 25-27 Oe) and nitroxyl radicals (a_N = 11-14 Oe), which, according to [10], appear as a result of transformations of the initially formed anion radicals [9, 11, 12].

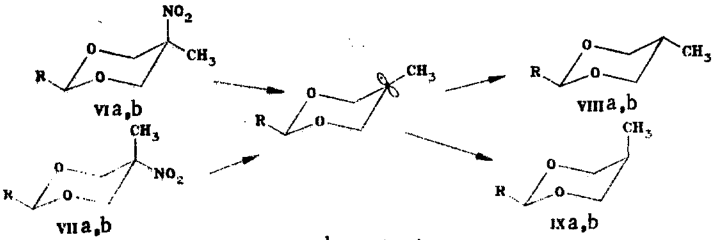


Thus, in contrast to aromatic anion radicals, aliphatic anion radicals IIa undergo further transformations with splitting out of potassium nitrite. The development of nitroxyl radicals in the process was also established in [13], in which the reduction of 5-alkyl-5-nitro-1,3-dioxanes with a solution of KOH in ethylene glycol was studied; 5-alkyl-1,3-dioxanes, 5-alkylidene-1,3-dioxanes, hydroxyacetaldehyde, and potassium nitrite were obtained.



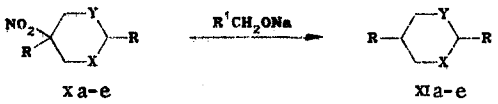
III—V a R=H; b R=CH_3; c R=C_2H_5; d R=C_3H_7

Mixtures of stereoisomeric 2,5-dialkyl-1,3-dioxanes IVb-d are formed in the case of 2-substituted 5-nitro-1,3-dioxanes IIIb-d [13, 14]. The ratios of the yields of the isomers do not depend on the three-dimensional structure of the starting 1,3-dioxanes VI and VII, evidently as a consequence of occurrence of the reaction through a step involving the formation of 2,5-dialkyl-1,3-dioxa-5-cycloalkyl radicals [13, 14].



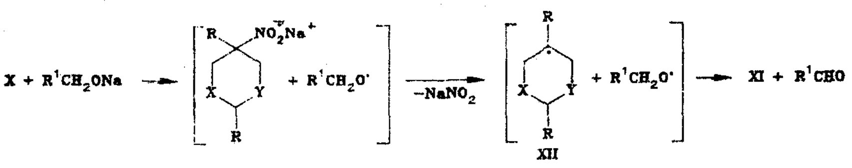
VI–IX a R=CH_3; b R=$CH(CH_3)_2$

5-Alkyl-1,3-diheterocycloalkanes XIa-e were obtained in 60-70% yields in the reduction of Xa-e with sodium alkoxides [14, 15].



X; XI a R=CH_3, b R=$CH(CH_3)_2$, c–e R=H; a–d X=O, e X=NCH_3; a,b Y=O, c–e Y=NCH_3

The synthetic value of this reaction consists in the fact that the easily synthesized nitro derivatives X can be converted in one step to the more difficult-to-obtain XI. The latter, according to [16], are formed as a result of electron transfer from the alkoxide to the nitro compound. Disproportionation of the resulting radicals in the "cage" leads to the final products:

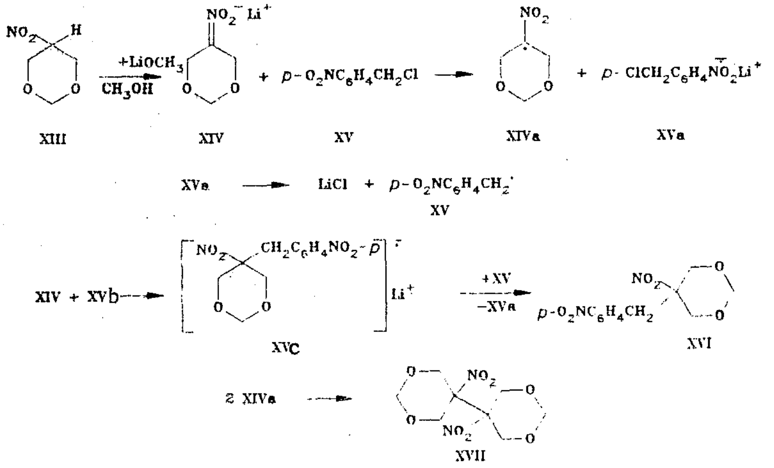


The reduction products are formed in part by detachment of hydrogen atoms by radicals XII. This is indicated by the development of recombination products, viz., 1,2-diols:

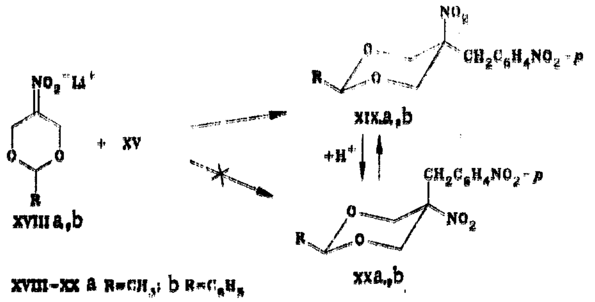
$$\mathrm{XII} + R'CH_2OH \longrightarrow \mathrm{XI} + R'\dot{C}HOH \longrightarrow R'CH(OH)CH(OH)R'$$

$$R'CH_2\dot{O} + R'CH_2OH \longrightarrow R'CH_2OH + R'\dot{C}HOH$$

The lithium salt of 5-nitro-1,3-dioxane (XIII) reacts with p-nitrobenzyl chloride in dimethylformamide (DMF) at 0°C to give benzyl-1,3-dioxane (XVI) and 5,5'-bis(5-nitro-1,3-dioxanyl) (XVII) [17]. A signal related to anion radical XVc was recorded by EPR spectroscopy of the reaction mixture [17]. The process is accelerated by UV irradiation and is retarded in the presence of free-radical acceptors [17]; this is characteristic for anion-radical reactions that proceed via an $S_{RN}1$ mechanism [18]. The results made it possible to propose the following scheme for the process [17]:



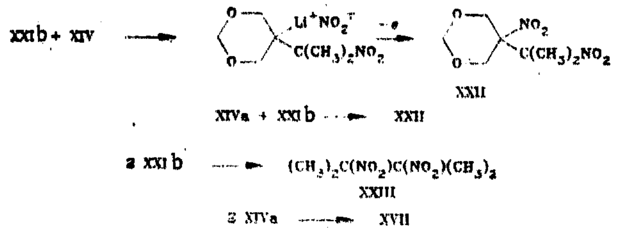
The formation of stereoisomers that differ with respect to the positions of the nitro group and the nitrobenzyl substituent is possible in the reaction of p-nitrobenzyl chloride with the lithium salts (XVIII) of 2-substituted 5-nitro-1,3-dioxanes. However, the formation of only an isomer with an axial nitro group was observed [17]. The stereospecificity of the reaction is associated with the greater accessibility of the equatorial position in lithium salts XVIII [17].



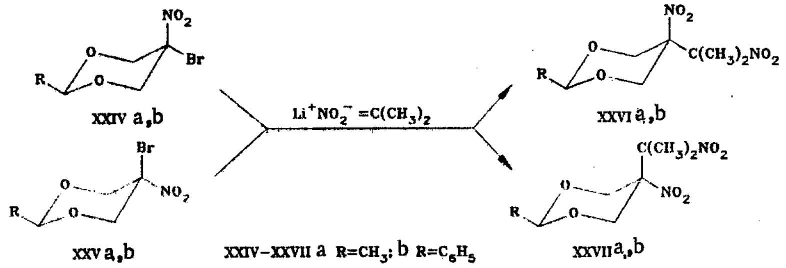
The reaction of 2-bromo-2-nitropropane (XXI) with salt XIV in dimethyl sulfoxide (DMSO) at 20°C gives dioxane XXII, bisdioxanyl XVII, and 2,3-dimethyl-2,3-dinitrobutane (XXIII) [18]. The reaction is accelerated by UV irradiation

$$\begin{tikzcd} \underset{XXI}{(CH_3)_2C(NO_2)Br} + XIV \arrow[r] & \underset{XXIa}{(CH_3)_2C(NO_2)^{\overline{\cdot}}Br} + XIVa \arrow[d] \\ & \underset{XXIb}{(CH_3)_2\dot{C}NO_2} + LiNO_2 \end{tikzcd}$$

and is retarded by electron acceptors. The presence of recombination products (dinitro compounds) in the reaction mixture indicates the formation of radicals XIVa and XXIb during the reaction [18, 19].

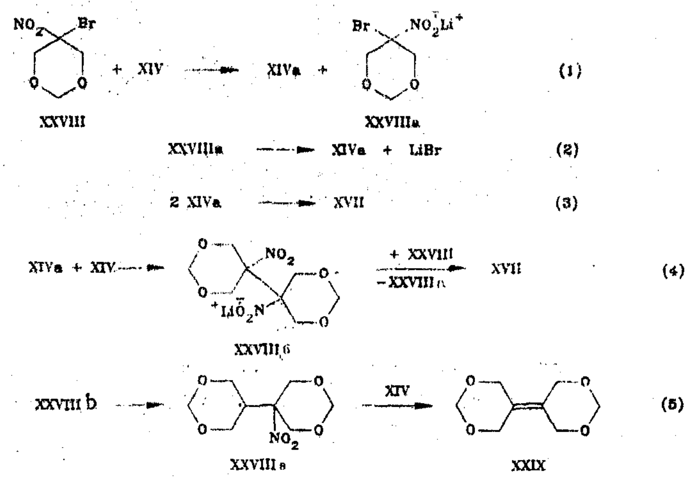


The reactions of individual stereoisomers of 5-bromo-5-nitro-1,3-dioxanes XXIV and XXV with the lithium salt of 2-nitropropane in DMSO at 20°C proceed stereoselectively with the primary formation of isomers XXVI with an axial nitro group [20]. It is interesting that the stereochemical result of the reaction is independent of the three-dimensional structures of the starting 1,3-dioxanes:

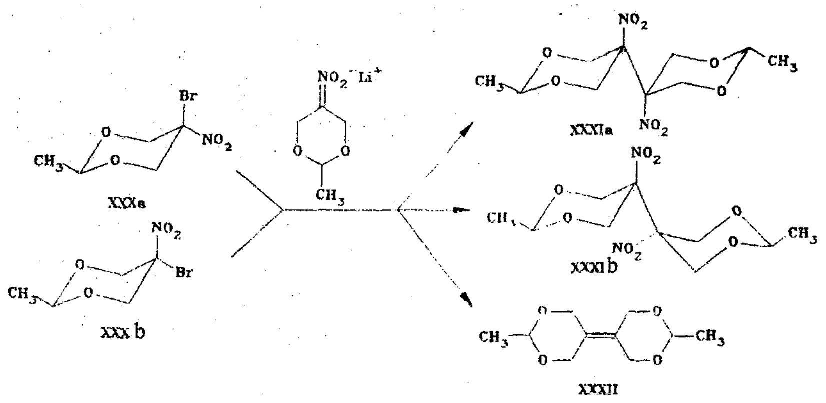


Lithium salts (XIV) of 5-nitro-1,3-dioxanes can act as nucleophilic agents in reactions with 5-bromo-5-nitro-1,3-dioxanes (XXVIII) [21, 22]. The reaction in DMSO leads to 5,5'-bis-(5-nitro-1,3-dioxanyl) (XVII) and 5,5'-bis(1,3-dioxanylidene) (XXIX).

The yields of XVII and XXIX depend on the ratios of the starting reagents. Thus the selectivity with respect to bisdioxanyl XVII increases with an increase in the concentration of substrate XXVIII [21]. It is apparent that in many respects the process is similar to the reaction of 2-bromo-2-nitropropane with the lithium salt of 5-nitro-1,3-dioxane.

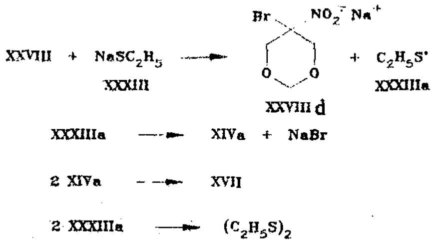


Mixtures of stereoisomeric 5,5'-bis(5-nitro-2-methyl-1,3-dioxanyls) and 5,5'-bis(2-methyl-1,3-dioxanylidenes) (XXXII) are formed in the reaction of individual 2-methyl-5-bromo-5-nitro-1,3-dioxanes with lithium salts of 5-nitro-2-methyl-1,3-dioxanes in DMSO at 20°C [22]:

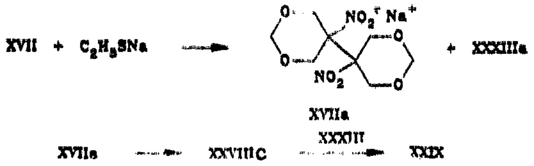


Primarily trans-stereoisomer XXXIa with a diaxial orientation of the two nitro groups is formed (in 52% yield): The yield of cis-isomer XXXIb is considerably lower (15%). The stereochemical result is independent of the three-dimensional structures of the starting dioxanes; this constitutes evidence in favor of an anion-radical pathway for the formation of the final products through a step involving 2-substituted 5-nitro-1,3-dioxa-5-cyclohexyl radicals.

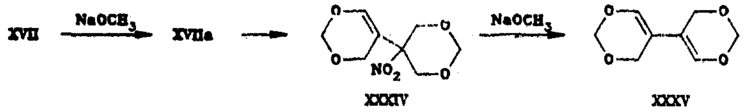
The reaction of 5-bromo-5-nitro-1,3-dioxanes XXVIII with sodium ethylmercaptide in DMSO at 20°C leads to 5,5'-bis(5-nitro-1,3-dioxanyl) (XVII), 5,5'-bis(1,3-dioxanylidene) (XXIX), and diethyl disulfide; sodium bromide and nitrite are also produced [23]. The reaction is also sensitive to UV irradiation and radical-reaction inhibitors; this made it possible to propose the following scheme:



When insufficient sodium ethylmercaptide is present, the reaction stops at the step involving the formation of dinitrobisdioxanyl XVII [23]. The latter, in the presence of excess ethylmercaptide undergoes further transformations to give 5,5'-bis(1,3-dioxanylidene) (XXIX) [23].

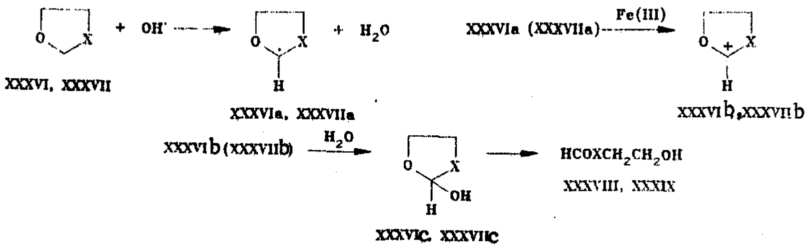


The reaction of 5,5'-bis(5-nitro-1,3-dioxanyl) (XVII) with sodium methoxide in DMSO at 20°C proceeds in a different direction and leads, when insufficient sodium methoxide is present, to 5-(5-nitro-1,3-dioxan-5-yl)-1,3-dioxane (XXXIV) and sodium methoxide and nitrite [24, 25]. Further transformation of nitro olefin XXXIV to 5,5'-bis(1,3-dioxene) (XXXV) occurs in the presence of excess sodium methoxide. The reaction is accelerated under UV irradiation; this confirms the anion-radical character of the process.



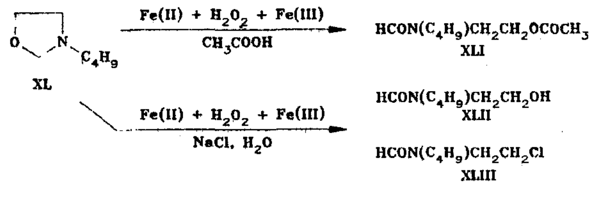
Reactions That Proceed through a Step Involving One-Electron Oxidation of 1,3-Diheterocycloalkyl Radicals

The loss of an electron upon reaction with Fe(III) [33, 34] was found to be characteristic for the 1,3-dihetero-2-cyclo-alkyl radicals that develop under the influence of redox systems [26-32]. Thus 1,3-dioxolane (XXXVI) and 3-propyloxazolidine (XXXVII) are converted to ethylene glycol monoformate (XXXVIII) and N-propyl-N-(2-ethoxyethyl)formamide (XXXIX) under the influence of Fe(II) + H_2O_2 + Fe(III) at 0-5°C in water. The formation of XXXVIII and XXXIX includes a step involving one-electron oxidation of the 1,3-dioxa- or 1-oxa-3-aza-2-cyclopentyl radicals.

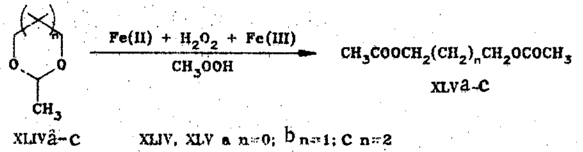


XXXVI, XXXVIII X=O; XXXVII, XXXIX X=N—C_3H_7

N-(2-Acetoxyethyl)-N-butylformamide (XLI, 60% yield) is formed in the reaction of 3-butyl-1,3-oxazolidine (XL) with the redox system in acetic acid, whereas N-butyl(2-chloroethyl)formamide (XLIII, 12% yield) is obtained along with N-butyl(2-hydroxyethyl)formamide (XLII, 45% yield) in a saturated aqueous solution of NaCl [34].

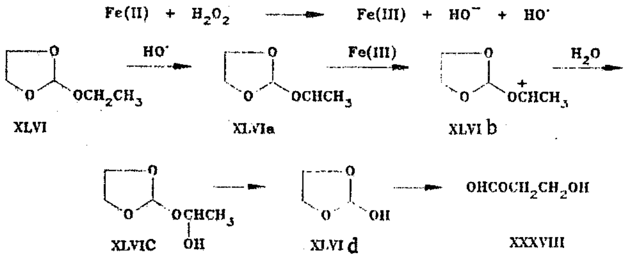


Upon reaction with the Fe(II) + H_2O_2 + Fe(III) system in acetic acid 2-methyl-1,3-dioxacyclanes XLIV give diacetates XLV [35].



Thus the nature of the nucleophilic particles present in solution determines the character of the resulting products.

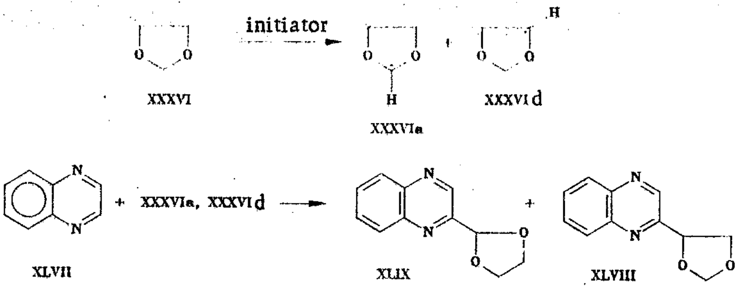
2-Ethoxyl-1,3-dioxolane (XLVI), which unexpectedly forms ethylene glycol monoformate (XXXVIII) and acetic anhydride, reacts somewhat differently with the Fe(II) + H_2O_2 + Fe(III) redox system [36]:



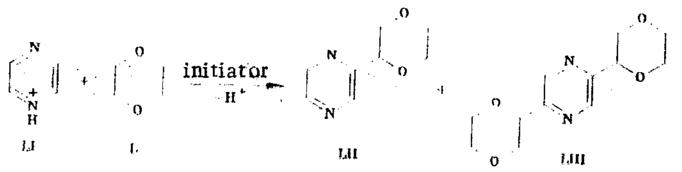
Similarly, the reaction of 2-ethoxy-1,3-oxathiolane leads to 2-mercaptoethyl formate [36]. One-electron oxidation of the monoalkoxyalkyl radicals is also the key step here.

Homolytic Replacement of a Hydrogen Atom in Protonated Hetero-aromatic Bases by a 1,3-Dioxacycloalkyl Residue

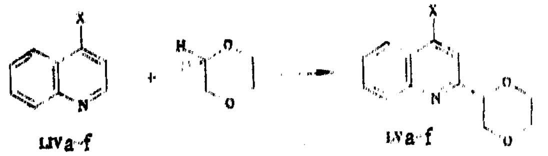
The nucleophilic properties of alkoxyalkyl and diakoxy-alkyl radicals have been used in the alkylation of protonated heteraromatic bases by them [37-39]. The formation of products of alkoxy- and dialkoxyalkylation of protonated heteroaromatic bases proceeds with the participation of cation radicals. It has been established [37] that 4-(2-quinoxalinyl)-1,3-dioxolane (XLVIII) is formed selectively in the reaction of 1,3-dioxolane (XXXVI) with quinoxaline (XLVII) in the presence of a source of tert-BuO· radicals, whereas 4- and 2-substituted dioxolanes XLVIII and XLIX are formed simultaneously under the influence of ·OH radicals.



1,4-Dioxane (L) reacts with the pyrazinium cation (LI) to give alkylation products LII and LIII [37]:

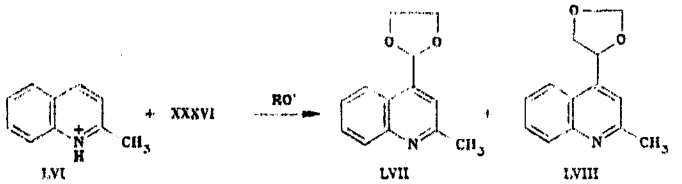


A quantitative evaluation of the relative reactivities of 4-substituted quinolines LIV in reactions with radicals generated from 1,4-dioxane demonstrated that electron-acceptor substituents promote an increase in the activity of the protonated base [37]. This dependence of the reactivities is explained by the fact that the transition state in reactions with nucelophilic 1,4-dioxanyl radicals is achieved more rapidly in the case of heterocycles that have greater electrophilicities.

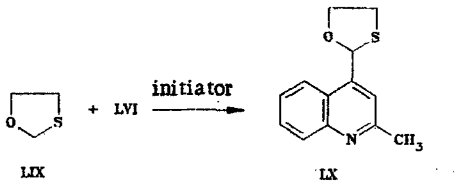


LIV, LV a X=H; b X=OCH_3; c X=CH_3; d X=Cl; e X=$COOC_2H_5$; f X=CN

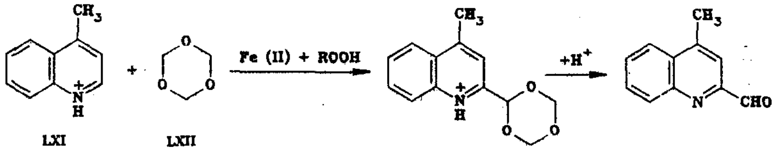
The reaction of 1,3-dioxolane with protonated quinaldine (LVI) initiated by ROOH + Fe(II) systems [R = $C(CH_3)_3$, $C_6H_5C(CH_3)_2$] leads chiefly to 2-substituted dioxolane LVII (72-78% yield) and, to a lesser extent, to 4-substituted 1,3-dioxolane LVIII (12-14% yield) [40]:



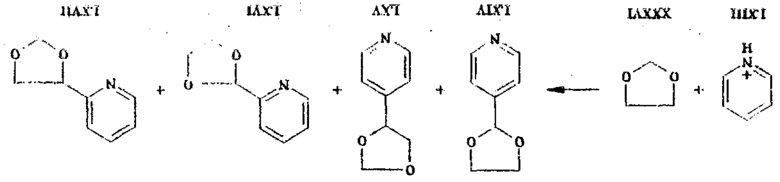
On passing to the Fe(II) + H_2O_2 system, which gives hydroxyl radicals, which are more active and less selective than tert-BuO' and $C_6H_5C(CH_3)_2O$', the probability of the formation of 1,3-dioxa-4-cyclopentyl radicals increases, as a result of which the yields of dioxolanes LVII and LVIII are 40% and 35%, respectively. The yield of the 2-substituted 1,3-dioxolane increases with an increase in the pH of the medium. The latter is associated with the fact that more nonhydrolyzed Fe^{3+} ions than hydrolyzed $Fe(OH)^{2+}$ ions are present in the system at low pH values, and the probability of one-electron oxidation — disappearance of the 1,3-dioxa-2-cyclopentyl radicals (with their subsequent conversion to ethylene monoformate) — is higher. In contrast to 1,3-dioxolane, only 2-methyl-4-(1,3-oxathiolan-2-yl)quinoline (LX) is formed in 90% yield in the reaction of 1,3-oxathiolane (LIX) with protonated quinaldine initiated by the $C_6H_5C(CH_3)_2OOH$ + Fe(II) system [41]. The high selectivity of formation with respect to 2-substituted 1,3-oxathiolanes is due to the high selectivity of the formation of 1-oxa-3-thia-2-cyclopentyl radicals from 1,3-oxathiolanes under the influence of oxygen-centered radicals.



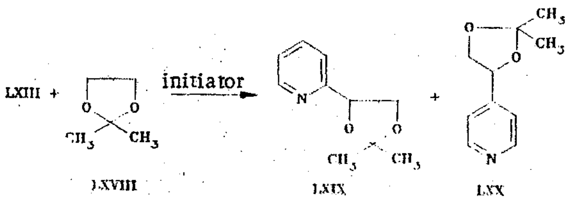
The reaction of 1,3,5-trioxane (LXII) with protonated 4-methylquinoline (LXI) has been used as a method for the introduction of a formyl group into a heteroaromatic base [39].



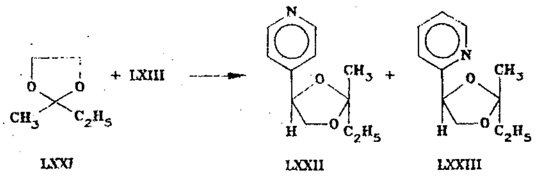
The regiospecificity and stereospecificity of the reaction of protonated pyridine with 1,3-dioxolanes have been studied [42]. The four possible regioisomers are formed when 1,3-dioxolane is used. Primarily isomers LXIV and LXVI, which are derivatives of 1,3-dioxa-2-cyclopentyl radicals, were obtained [42]. The sum of the yields of isomers LXVI and LXV is greater than the sum of the yields of LXVI and LXVII, which constitutes evidence for the higher reactivity of the 4 position of the pyridinium cation with respect to nucleophilic dioxolanyl radicals.



Only two isomers, viz., LXIX and LXX, which are derivatives of 2,2-dimethyl-1,3-dioxa-4-cyclopentyl radicals, are formed in the case of 2,2-dimethyl-1,3-dioxolane (LXVIII).



2-Methyl-2-ethyl-1,3-dioxolane (LXXI) can react with protonated pyridine to give two regioisomers, each of which exists in the form of a pair of stereoisomers. It was estabished that only trans-2-methyl-4-(4-pyridyl)-2-ethyl-1,3-dioxolane (LXXII) and trans-2-methyl-4-(2-pyridyl)-2-ethyl-1,3-dioxolane (LXXIII) are formed under the reaction conditions (0-5°C, pH 4-5).



The formation of only trans isomers is associated with their greater thermodynamic stability as compared with the cis isomers, which are capable of epimerization under the reaction conditions (pH<7) [43].

The results presented above make it possible to regard the ion-radical and redox transformations of 1,3-dioxacyclanes as a highly effective method for their functionalization. In virtually all cases these processes are realized under mild conditions and are distinguished by high yields and selectivity; this opens up possibilities for the substantial expansion of the synthetic chemistry of cyclic acetals.

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EFFECT OF THE HETEROATOM OF A BENZO[b]-ANNELATED FIVE-MEMBERED HETERORING ON THE STRUCTURE AND PROPERTIES OF AN AMINOVINYL KETONE FRAGMENT INCLUDED IN THE RING

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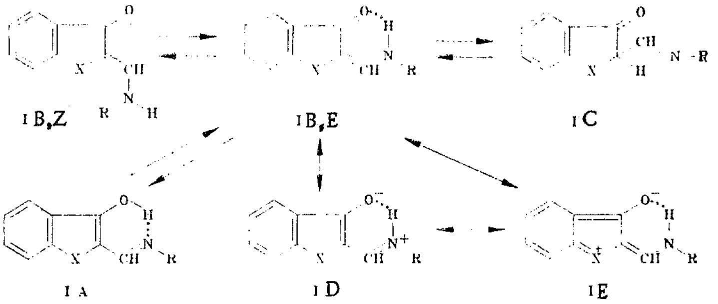
An analysis of the results of theoretical and physicochemical studies of and x-ray diffraction data for a series of aminovinyl ketones — derivatives of hydroxy aldehydes of benzo[b]-annelated five-membered heterosystems — is presented. In addition to the peculiarities of the aminovinyl ketone fragment, the effect of the heteroatom of the five-membered ring on the structure and properties of aminovinyl ketones, which consists in direct electronic conjugation of the ring carbonyl group with the heteroatom, was ascertained.

Studies carried out by means of electronic, IR, and PMR spectroscopy [1-3] and x-ray diffraction analysis [4-6] have made it possible to establish and confirm, by means of the results of quantum-chemical calculations [7], the preferableness of an aminovinyl ketone structure (B) for the potentially tautomeric molecules of the I type in the solid phase and in various solvents, regardless of the external conditions (temperature, irradiation). It has also been shown that some types of aminovinyl ketones exist in solutions in the form of two (E and Z) equilibrium forms [2, 8-10], and opinions regarding the preferableness of the $O^{-}-CR=CR-CH=N^{+}HR$ zwitter-ion structure in the aminovinyl ketone fragment have been expressed [10-13].



In the present communication we attempted to evaluate the peculiarities of the structure of compounds of the I type and their derivatives as a function of the properties of the structural links, particularly the X group of the five-membered ring. The IB molecules may exist in the form of Z-IB and E-IB isomers [with an intramolecular hydrogen bond (IMHB)], each of which, as a consequence of the effects of conjugation of the electron-acceptor carbonyl group, contains a certain degree of contribution of canonical forms D and E. Structure D reflects π polarization in the tautomeric chain. The contribution of the E form, which corresponds to π interaction of the C=O and X groups, will increase with an increase

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