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ON DIOXOLANATION REACTION OF CYCLOHEX-3-ENE-1-CARBALDEHYDES WITH 1,2-DIOLS AND PROPERTIES OF PREPARED PRODUCTS**A.Kh. Kerimov, A.T. Orudzheva, Kh.A. Mamedova***Institute of Polymer Materials of Azerbaijan National Academy of Sciences
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Generalized results of the analysis of synthesis reaction of cyclic acetals of 1,3-dioxolane series by condensation of cyclohex-3-ene-1-carbaldehydes with 1,2-propanediol and its 3-chloro-, 3-chloroalkoxy derivatives, as well as their epoxidation, bromination, dichlorocarbonylation on C=C bond of cycle and dienophilic activity were presented. The influence of the nature of substituents on relative reactivity of reacting components and efficiency of the prepared products as the ED-20-based active diluent of the polymer composition has been considered.

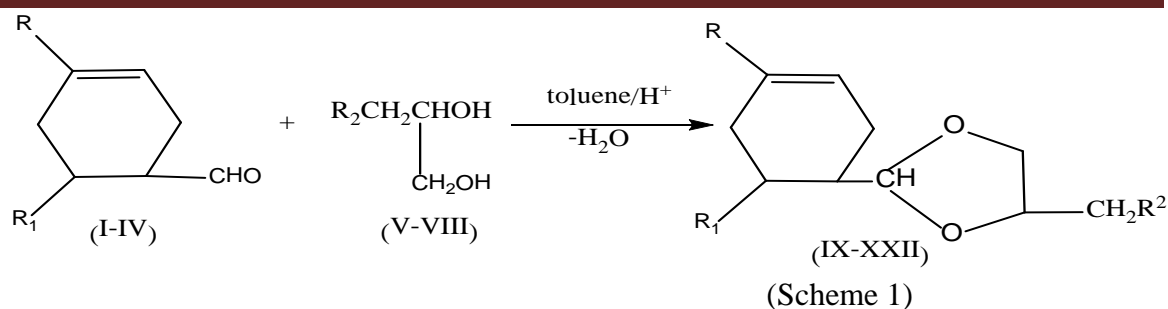
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The reaction of vicinal diols with carbonyl addends is an accessible method of synthesis of five-membered heterocycles with vicinal dioxogroups – 1,3-dioxolanes [1-3]. The cyclic acetals of 1,3-dioxolane series are applied as plasticizers [4], modifiers [5], solvents of cellulose esters [6], metal corrosion inhibitors [7] and substances intensifying oil extraction [8] etc. In addition, they are of the utmost interest as perspective monomers for polymerization processes [9]; intermediate compounds in the synthesis of biologically active and pharmaceutical preparations [10]. It should be noted that an additional interest to this class of compounds stimulated an opening of anti-HIV activity of some preparations prepared on the basis of substances containing 1,3-dioxolane cycle [11, 12]. However, there are very few reports in the literature devoted to the synthesis of 1,3-dioxolanes from aldehydes having unsaturated carbocyclic substituents in line with the cyclohexene structure while

current works have often sporadic nature [13, 14]. Consequently, the involvement of 1,3-dioxolane derivatives, cyclohex-3-ene-1-carbaldehydes, on the one hand, and functionally substituted 1,2-propanediol derivatives, on the other hand, not only allows expanding their assortment but also puts forward an important task – establishment of the relative reactivity of the reacting components depending on the electronic and spatial factors stipulated by their substituents.

The work provides the generalized information on the analysis of synthesis of 2,4-disubstituted 1,3-dioxolanes by interaction of cyclohex-3-ene-1-carbaldehyde (I), its 4-methyl- (II), 6-methyl- (III) and 4,6-dimethyl derivatives (IV) with 1,2-propane diol (V) and its 3-chloro- (VI), 3-(2-chloroethoxy)- (VII), 3-(1,3-dichloropropoxy) derivatives (VIII) in the presence of ion-exchange resin KU-2 (H⁺ – form) as appears from the scheme below:



R=R₁=H (I); R=CH₃, R₁=H (II); R=H, R₁=CH₃ (III); R=R₁=CH₃ (IV).

R₂=H (V); Cl (VI); ClCH₂CH₂O (VII); (ClCH₂)CHO (VIII).

R=R₁=R₂=H (IX); R=CH₃, R₁=R₂=H (X). R₂=Cl: R=R₁=H (XI); R=CH₃, R₁=H (XII); R=H, R₁=CH₃ (XIII); R=R₁=CH₃ (XIV).

R₂= ClCH₂CH₂O: R=R₁=H (XV); R=CH₃, R₁=H (XVI); R=H, R₁=CH₃ (XVII); R=R₁=CH₃ (XVIII).

R₂= (ClCH₂)₂CHO: R=R₁=H (XIX); R=CH₃, R₁=H (XX); R=H, R₁=CH₃ (XXI); R=R₁=CH₃ (XXII).

The reaction course was controlled by means of GLC method— by fixation of concentration change in the base product over time [15]. The method of internal standard [15] was used for quantitative calculation of the conversion of initial components into the base product. On chromatograms the components of reaction mixture [as an example of synthesis of compound (XI)], are placed according to their retention time in the following sequence: toluene (solvent), cyclohex-3-ene-1-carbaldehyde, 3-chloro-1,2-propanediol, dimethyl phthalate (standard) and 2-(3-cyclohexenyl)-4-chloromethyl-1,3-dioxolane. According to GLC analysis, each of the synthesized 2,4-disubstituted compounds (IX-XXII) is a mixture of cis- and trans-isomers with ratio of 55-45 %. We failed to isolate the separate isomers from their mixture; however, the PMR-spectroscopy data reaffirm the availability of these isomers notable for the arrangement of substituents on either sides of the five-membered rigid heterocycle [16].

With the aim of examining the nature of substituents of initial diols on their relative reactivity in the reaction with aldehyde (I) it was introduced diol (V) (taken as a standard) and its above-listed chloro- and chloroalkoxy derivatives (VI-VIII). It was established that in the optimal conditions [17] an initial rate ($W_0 \cdot 10^4$) of the formation reaction of dioxolane (XI) from diol (VI) is 5.60 ± 0.48

mol/(l.s.) (calculations were carried out by least-squares method [18]) and more than two times exceeds the same index of the formation reaction of dioxolane (IX) from diol (V) [2.75 ± 0.22 mol/(l.s.)] which is apparently a logical consequence of the influence of the inductive effect of the electron-acceptor substituent (Cl) coupled with field effect [19]. Since the chlorine atom and primary OH group in a diol molecule (VI) are at peripheral atoms of unsaturated chain (consisting of three carbon atoms), and transfer of the inductive effect in such saturated systems is rapidly fading [see [19] p. 31-37], the observed effective transfer of the latter can be realized only with the participation of the field effect, i.e. according to the Newman projection formulas, (φ^1 -) beveled conformer (20) is energetically more advantageous out of three possible odd conformations of diol (VI) (φ^1 , φ^3 , φ^5).

A geometry of the latter one favors the formation of the hydrogen bond between chlorine atom and hydrogen atom of primary OH group of diol (VI), which apparently facilitates not only approach of nucleophile (VI) to substrate (I), but also elimination of water molecule from protonated hemiacetal (A) (scheme 2).

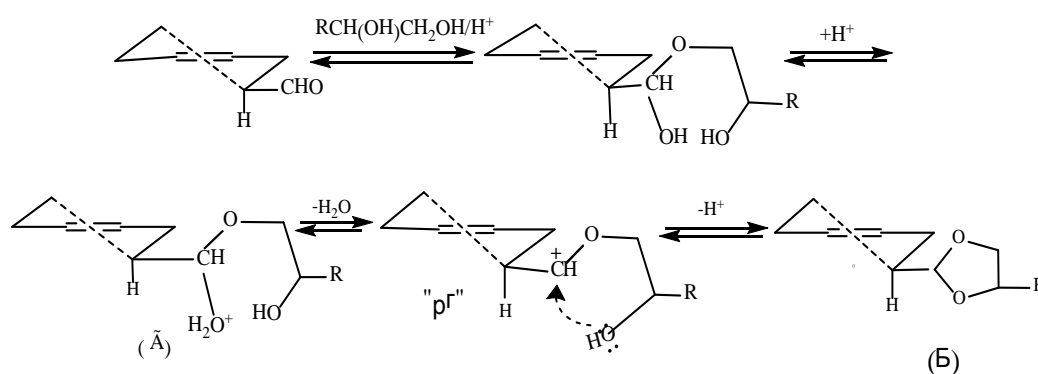
However, when introducing more voluminous electron-acceptor substituents (ClCH₂CH₂O) or [(ClCH₂)₂CHO] in the

methyl group of diol (V), an initial rate ($W_0 \cdot 10^4$) of the formation reaction of compounds (XV, XIX) from diols (VII, VIII) and aldehydes (I) is 3.95 ± 0.32 and 2.65 ± 0.19 mol/(l.s.), respectively. Note that the generalization of the obtained data of

the initial rates of the interaction reaction of 1,2-propanediol and its above-listed chloro-, chloroalkoxy derivatives (VI – VIII) with the same aldehyde (I) [2.75, 5.60, 3.95 and 2.60 mol/(l.s.)] respectively shows that as the volume of substituents introduced in methyl group of diol (V) rises, the reaction rate subsequently runs low and in a case of diol (VIII) it comes short of the same index in the formation reaction of dioxolane (IX) from diol

(V). Consequently, in case of the possibility of electron and spatial factors' influence on relative reactivity of the initial diols, the latter is decisive [see [19]. p. 37].

When generalizing the kinetic data obtained, it is possible to conclude that the analyzed reaction is reversible and described by kinetic equation of the second order [18]. Based on these determinations and given the that the mechanism of dioxolanation with regard to aldehydes of cyclohexene series with 1,2-diols has not thoroughly been in the literature and using the conformation of the semi-armchair of the cyclohexene ring (see [20], p. 456), we assume that the reaction proceeds according to the scheme described below (with reference to literature [21]:

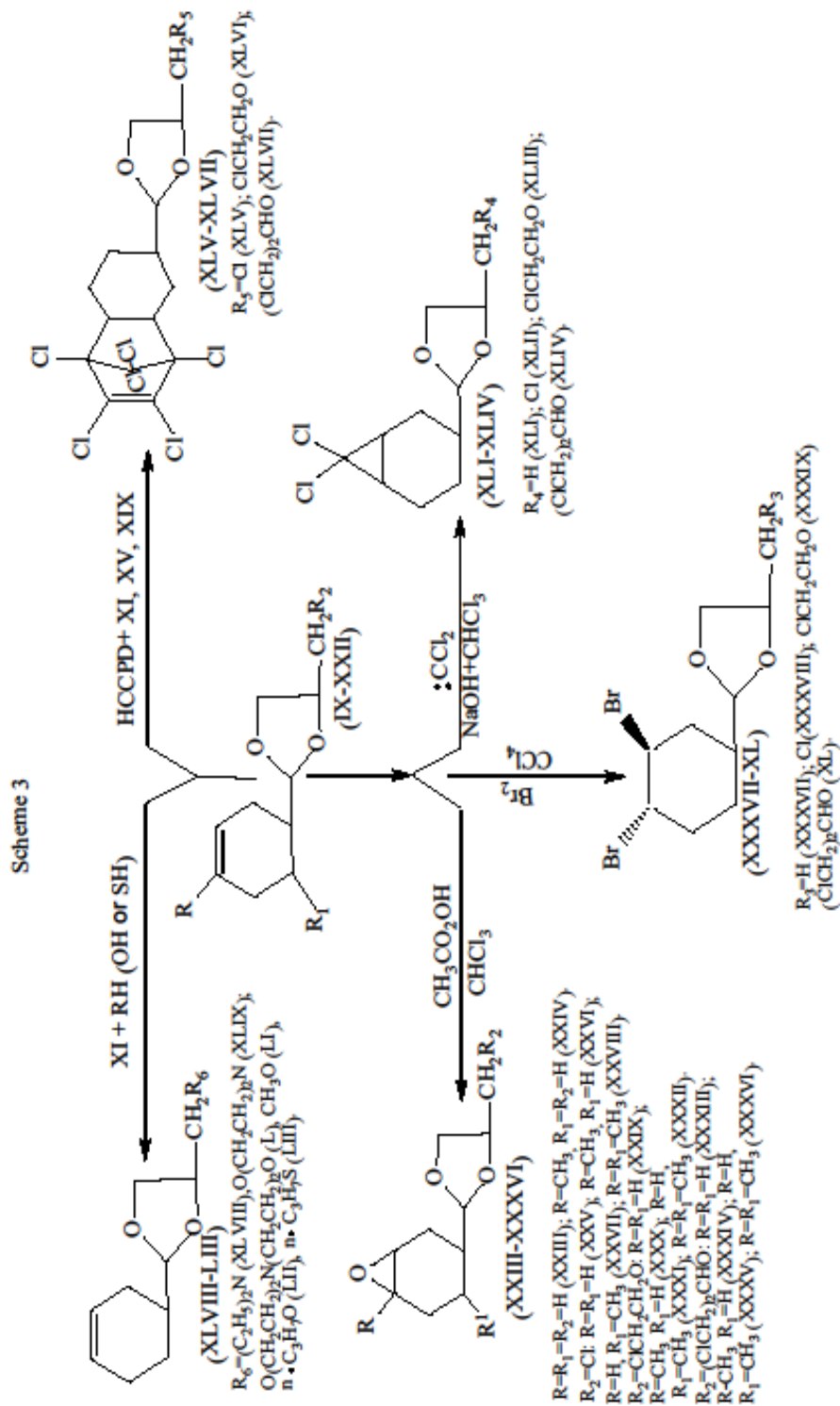


(Scheme 2)

Since the initial stage of the reaction formation mechanism of acetals of 1,3-dioxolane series (realized by interaction of aldehydes with 1,2-diols) is identical to the mechanism of the acyclic acetals preparation reaction [21], the subject of discussion in this case can be only the cyclization process of intermediate (or so-called resonance hybrid (RH)) (scheme 2) with formation of the basic product (B), i.e. according to the proposed mechanism (scheme 2) the protonated hemiacetal (A) losing water molecule (with participation of an electron pair in the neighboring oxygen atom) is converted into "RH". Then, there is an apparent attack of carbocation in "RH" with lone-electron pair of carbon atom of "OH" group and as a result a bond "O-H" is weakened and after a proton is

torn away the cycle formation is over (scheme 2).

Relatively alternative variants of cyclization "RH" are presented in the work [21]. It should be noted that the implementation of cyclization with conversion of "RH" in enol ether is impeded due to unlikelihood of proton's tearing away from sp^3 of the hybridized carbon atom of carbocycle in these conditions. Consequently, the implementation of cyclization through enol ether would lead to extremely low yields of the corresponding basic product which is contrary to the experimental data [22-25]. The incapacity of cyclization by means of formation of intermediate with endo-carbon-oxygen double bond was convincingly proved in the work [21], based on Baldwin rule for ring closure [26].



The supposed reaction mechanism (scheme 2) is in accordance with experimental data that makes it possible to explain the influence of the electron and steric factors caused by an appropriate substituent on relative reactivity of the initial diols.

Owing to the fact that the aldehyde group in the conformation of the semi-armchair of cyclohex-3-ene-1-carbaldehyde and its above-listed methyl substituted homologs (II-IV) has a real equatorial orientation (see [20] p. 456), an attack of its protonated intermediate by corresponding nucleophile (V-VIII) is essentially facilitated and consequently, an availability of the methyl group in position 4C , 6C of carbocycle has no effect on its reactivity.

It revealed that an oxidation of the compounds (IX-XXII) by 50 % aqueous solution of peroxyacetic acid leads to the corresponding epoxy-derivatives (XXIII-XXXVI) (scheme 3) with good yields while an example of conjunctive bromination and dichlorocyclopropanation of the compounds (IX, XI, XV и XIX) makes it possible to synthesize their corresponding trans-dibromo- (XXXVII-XL) and gemdichloromethylene derivatives (XLI-XLIV). Further, as an example of condensation of the compounds (XI, XV and XIX) with hexachlorocyclopentadiene it found the possibility of their application as dienophile which allows to synthesize the polychlorine-containing derivatives of 1,3-dioxolanes with norbornene fragment (XLV-XLVII). It showed by the example of the compound (XI) that the chlorine atom in the chloromethyl side-chain of 1,3-dioxolanes of cyclohexene series is notable

for high mobility and easily substituted for amino- (XLVIII-L), alkoxy алкокси- (LI, LII), propylthiogroup (LIII) which allows to expand the assortment of functionally substituted five-membered heterocycles with vicinal dioxagroups.

The above-mentioned characteristic chemical conversions of the synthesized compounds (IX-XXII) determining their synthetic possibilities in the generalized form are presented in scheme 3. The synthesized 2,4-disubstituted 1,3-dioxolanes (IX-XXII) and products of their conversion (XXIII-LIII) are odourless, transparent liquids. They are insoluble in water, well dissolved in organic solvents (acetone, ether, ethanol, etc). The physical-chemical constants, as well as data of elemental analysis and spectral indices of the synthesized compounds (IX-XXII) and products of their conversion (XXIII-LIII) were offered in the work [22] and following publications [1, 3, 4, 17, 22-25]. Owing to the fact that the creation of polymer composition materials with high operational properties based on industrial epoxide resins is topical, especially as it becomes increasingly important with the growth of technological progress, as exemplified by some representatives among the synthesized compounds (XLV-XLVII). It revealed the possibility of their application as an active diluent (modifier) hardened by polyethylene polyamine (PEPA) of epoxy diene composition based on the industrial epoxy diene resin ED-20. The description of experiment and physical-mechanical characteristics of the prepared composition materials were presented in the publication [4].

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**TSİKLOHEKS-3-EN-1-KARBALDEHİDLƏRİN 1,2-DİOLLAR İLƏ DİOKSOLANLAŞMASI
REAKSİYASI VƏ ALINAN BİRLƏŞMƏLƏRİN XASSƏLƏRİ HAQQINDA**

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Tsikloheks-3-en-1-karbaldehidlərin 1,2-propandiol və onun 3-xlor-, 3-xloralkoksi törəmələri ilə kondensləşməsi reaksiyası əsasında 1,3-dioksolan sırası tsiklik asetalların sintezi, onların epoksidləşmə, bromlaşma, dixlorkarbenilləşmə və dienofil fəallığının müəyyən edilməsi istiqamətində aparılmış tədqiqatların ümumiləşdirilmiş təhlili verilmiş və eləcə də qarşılıqlı təsirdə olan komponentlərin əvəzləyicilərinin təbiətinin onların nisbi reaksiya qabiliyyətinə təsiri araşdırılmışdır. Həmçinin alınan birləşmələrin ED-20 qatranı əsasında hazırlanan polimer kompozisiyalarının fəal durulaşdırıcısı kimi effektivliyinin öyrənilməsi və əldə edilən nəticələr şərh edilmişdir.

Açar sözlər: *visinal dioksoqrup saxlayan beşüzvlü heterotsikllər, reaksiya sürəti, nisbi reaksiya qabiliyyəti, dioksolanlaşma reaksiyasının mexanizmi.*

О РЕАКЦИИ ДИОКСОЛАНИРОВАНИЯ ЦИКЛОГЕКС-3-ЕН-1-КАРБАЛЬДЕГИДОВ С 1,2-ДИОЛАМИ И СВОЙСТВАХ ПОЛУЧЕННЫХ ПРОДУКТОВ

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Приведены обобщенные результаты исследования реакции синтеза циклических ацеталей 1,3-диоксоланового ряда конденсацией циклогекс-3-ен-1-карбальдегидов с 1,2-пропандиолом и его 3-хlor-, 3-хlorалкоксипроизводными, а также их эпоксидирование, бромирование, дихlorкарбенилирование по С=С связи цикла и диенофильной активности. Рассмотрено влияние природы заместителей на относительную реакционную способность реагирующих компонентов и эффективность полученных продуктов в качестве активного разбавителя полимерной композиции на основе ЭД-20.

Ключевые слова: *пятичленные гетероциклы с вицинальными диоксогруппами, скорость реакции, относительная реакционная способность, механизм реакции диоксоланирования.*