SYNTHESIS AND REACTIVITY OF ETHOXYVINYL DERIVATIVES OF 1,3-DIOXOLANIUM SALTS

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2-(β-Ethoxyvinyl)dioxolanium salts were obtained by reaction of ortho esters with 2,4,4,5,5-pentamethyl-1,3-dioxolanium perchlorate in acetic anhydride. Alkaline hydrolysis of 2-(β-ethoxyvinyl)-4,4,5,5-tetramethyl-1,3-dioxolanium perchlorate leads to the corresponding α,β-unsaturated aldehyde. Substituted 2-(β-aminovinyl)-1,3-dioxolanium perchlorates are formed by reaction of this salt with aromatic amines, amino acids, and urea. These perchlorates readily split out perchloric acid in alkaline media to give Schiff bases. The charges and electron densities were calculated for the 2-(β-methoxyvinyl)-1,3-dioxolanium cation.

The methyl (or methylene) group of 2-alkyl-1,3-dioxolanium salts has proved to be active in condensation reactions with acetals of aromatic and heterocyclic aldehydes [1]. Proceeding from this it might have been assumed that a similar reaction should also occur in the ortho ester series, since they are similar to acetals with respect to their structure and properties.

It was found that the reaction of ortho esters with dioxolanium salts actually proceeds very readily on heating equimolecular amounts of the reagents in excess acetic anhydride to give 2-β-ethoxyvinyl derivatives (III, Table 1). The first step in this transformation is apparently dissociation of the dioxolanium salt under the influence of increased temperature and a solvent to give reactive methylene pseudobase I. The perchloric acid that forms in the reaction reacts with the ortho ester, and this leads to the formation of diethoxycarbonium salt II [2]. The reaction of base I with salt II and subsequent splitting out of a molecule of alcohol leads to ethoxyvinyl compound III.

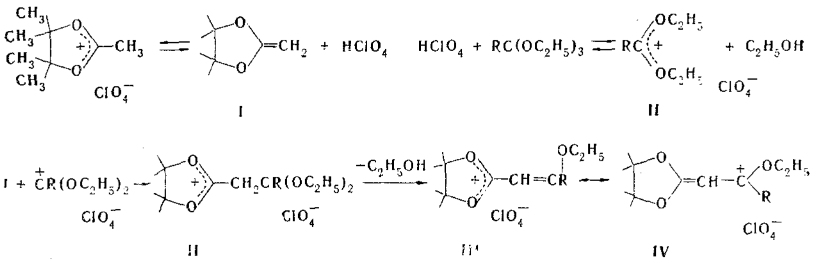

TABLE 1. 2-(β-Ethoxyvinyl)-1,3-dioxolanium Perchlorates (III)

Compound	R	R′	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	Cl	C	H	Cl	
IIIa	H	C_2H_5	110	$C_{11}H_{19}ClO_7$	44,4	6,3	11,7	44,2	6,4	11,9	87
IIIb	CH_3	C_2H_5	47	$C_{12}H_{21}ClO_7$	46,5	6,6	11,2	46,1	6,7	11,4	78
IIIc	C_2H_5	C_2H_5	116	$C_{13}H_{23}ClO_7$	48,0	7,0	10,6	47,8	7,0	10,9	62
IIId	C_6H_5	CH_3	107	$C_{16}H_{21}ClO_7$	53,6	5,6	9,6	53,3	5,8	9,8	45

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TABLE 2. Charges and Electron Density in the Boundary Orbital for the 2-(β-Methoxyvinyl)-1,3-dioxolanium Cation

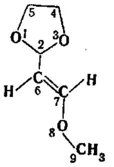
Structure	Atom No.	Overall charge	Charge in the π-system	Density in the boundary MO
	1	−1,0179	+0,082	0,1084
	2	+1,5717	+0,532	1,1428
	3	−1,0162	+0,081	0,1084
	4	+0,5021		
	5	+0,5023		
	6	−0,1565	−1,108	0,0090
	7	+0,8160	+0,059	0,9000
	8	−0,9749	+0,084	0,1020
	9	+0,4211		

TABLE 3. 2-(β-Aminovinyl)-1,3-dioxolanium Perchlorates (VIII)

Compound	R	R′	mp, °C	Empirical formula	Found, %			Calc., %			Yield, %
					C	H	Cl	C	H	Cl	
VIIIa	H	*p*-OCH_3	185	$C_{16}H_{22}ClNO_7$	51,2	6,0	9,3	51,1	5,8	9,4	90
VIIIb	H	H	155—156	$C_{15}H_{20}ClNO_6$	52,0	5,8	10,3	52,1	5,8	10,3	87
VIIIc	H	*o*-OCH_3	133	$C_{16}H_{22}ClNO_7$	51,1	5,9	9,2	51,1	5,8	9,4	98
VIIId	H	*p*-CH_3	168	$C_{16}H_{22}ClNO_6$	53,9	6,4	9,8	53,4	6,1	9,9	80
VIIIe	H	*p*-OC_2H_5	168—169	$C_{17}H_{24}ClNO_7$	52,6	6,2	9,2	52,4	6,2	9,1	95
VIIIf	H	*o*-Cl	118	$C_{15}H_{19}Cl_2NO_6$	47,4	5,2	18,5	47,4	5,0	18,7	98
VIIIg	H	*m*-Cl	199	$C_{15}H_{19}Cl_2NO_6$	47,8	5,5	18,7	47,4	5,0	18,7	92
VIIIh	H	*o*-COOH	172,5[a]	$C_{16}H_{20}ClNO_8$	49,1	5,3	8,5	49,3	5,1	9,1	95
VIIIi	H	*p*-COOH	230[a]	$C_{16}H_{20}ClNO_8$	49,6	5,7	9,2	49,3	5,1	9,1	98
VIIIj	H	*p*-SO_2NH_2	192[a]	$C_{15}H_{21}ClN_2O_8S$[b]	42,5	4,9	8,2	42,4	4,9	8,4	83
VIIIk	H	*p*-$SO_2NHC_3H_2NS$	188—189[c]	$C_{19}H_{22}ClN_3O_7S$[d]	47,8	4,6	7,8	48,3	4,7	7,5	91
VIII*l*	CH_3	*p*-OCH_3	142	$C_{17}H_{42}ClNO_7$	52,3	6,1	8,7	52,4	6,2	9,1	90

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[a] With decomposition.

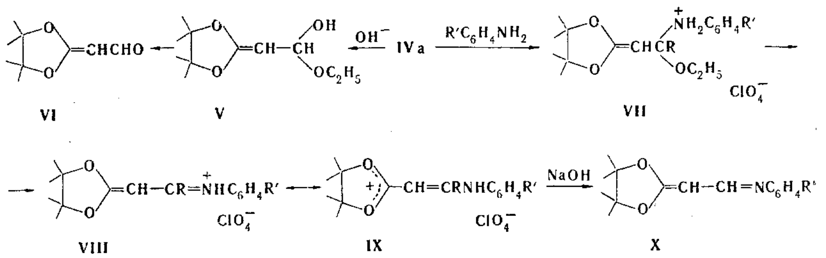
[b] Found: S 7.4%. Calculated: S 7.5%.

[c] C_3H_2NS is 2-thiazolyl.

[d] Found: S 7.7%. Calculated: S 6.8%.

A similar mechanism was adopted for the reaction of ortho esters with the quaternary salts of nitrogen heterocycles in the synthesis of cyanine dyes [3].

It is well known that dioxolanium salts readily react exclusively with various nucleophiles (water and alcohol) with opening of the dioxolanium ring [4]. However, the behavior of the 2-ethoxyvinyl derivative that we investigated differs substantially in such reactions. Attack of the nucleophile on reaction with alkali and during aminolysis is directed to the positively charged β-carbon atom of the ethoxyvinyldioxolanium salt (mesomeric form IV).



The results of calculations of the total charges (σ+π) on the atoms in the 2-(β-methoxyvinyl)-1,3-dioxolanium cation, which were obtained by the extended Hückel method, are presented in Table 2, and the charge distribution in the π system of the fragment of interest in the molecule is derived. The geometric characteristics of the molecule were taken in accordance with the standard bond lengths and valence angles [5], the orbital exponents were calculated by the Slater method, and the valence-bond ionization potential values were taken from the report in [6].

It follows from these data that the greatest positive charge is located on the central carbon atom of the ring rather than on the β-carbon atom.

The electron density in the boundary MO should serve as a more accurate characteristic of the nucleophilic reactivity [7]. The MO_{26} orbital is an orbital of the π type.

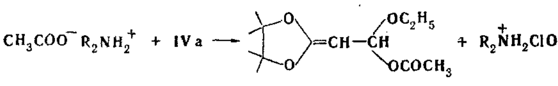
It can be seen (Table 2) that although the ring carbon atom is as before expected to be the most active center with respect to nucleophilic attack, the difference in the reactivity indexes for this carbon atom and the β-carbon atom is leveled off. Since the β-carbon atom is sterically shielded to a lesser degree, preferred reaction with transfer of the reaction center to the carbon atom in the β position relative to the dioxolanium ring becomes possible.

Addition products V and VII that are formed in this case are stabilized by splitting out of a molecule of alcohol to give α,β-unsaturated aldehyde VI or substituted 2-(β-aminovinyl)-1,3-dioxolanium salts VIII (Table 3).

Aromatic amines (with electron-donor and electron-acceptor substituents), amino acids, and urea undergo reaction with IIIa. On treatment with alkali the compounds thus obtained readily split out perchloric acid to give the corresponding Schiff bases (X) rather than enamines.

The IR spectra of perchlorates VIII contain intense absorption bands at 1650-1660 cm^{-1}, which probably correspond to the stretching vibrations of the polarized C=N bond; this attests to the predominant contribution of the mesomeric structure VIII as compared with IX.

Aliphatic amines and guanidine react with 2-ethoxyvinyl-substituted dioxolanium salts to give the perchlorates of these amines and mixed acetal acetate XI.



XI

This sort of direction of the reaction is apparently explained by the considerably higher basicity of the amines listed above as compared with their aromatic analogs. The concentration of free amine under the reaction conditions (acetic acid) is therefore lower than the concentration of the acetate ion, which attacks the β-carbon atom of the ethoxyvinyldioxolanium salt.

EXPERIMENTAL

The IR spectra of the substances obtained (in mineral oil suspensions) were recorded with a UR-20 spectrometer.

2-(β-Ethoxyvinyl)-4,4,5,5-tetramethyl-1,3-dioxolanium Perchlorate (IIIa). A 4-ml (0.04 mole) sample of acetic anhydride and 2 ml (0.013 mole) of freshly distilled ethyl orthoformate were added to 2.43 g (0.01 mole) of 2,4,4,5,5-pentamethyldioxolanium perchlorate [8], and the mixture was heated carefully until the salt had dissolved completely. It was then cooled and diluted with ether to give 2.6 g (87%) of light-yellow crystals with mp 110°. IR spectrum: 1100, 1245, 1380, 1460, 1528, 1610 cm^{-1}.

Compounds IIIb-d- (Table 1) were similarly obtained as difficult-to-crystallize light-yellow crystals that were readily hydrolyzed in air.

2-Formylmethylene-4,4,5,5-tetramethyl-1,3-dioxolane (VI). A 0.6-g (0.002 mole) sample of IIIa was shaken with 5 ml of 5% NaOH solution and 10 ml of ether. The ether layer was separated, and the ether was evaporated to give 0.31 g (91%) of colorless crystals with mp 113° (from petroleum ether). IR spectrum: 1140, 1380, 1460, 1600, 1650 cm^{-1}. Found: C 63.5; H 8.2%. $C_9H_{14}O_3$. Calculated: C 63.5; H 8.2%.

2-[β-(p-Methoxyanilino)vinyl]-4,4,5,5-tetramethyldioxolanium Perchlorate (VIIIa). Acetic acid solutions of 1.5 g (0.005 mole) of IIIa and 0.62 g (0.005 mole) of p-anisidine were mixed, and the mixture was allowed to stand for 5 min. It was then diluted with a small amount of ether and filtered to give 1.7 g (90%) of VIIIa as yellow needles with mp 185° (from acetic acid). IR spectrum: 1110, 1378, 1460, 1510, 1577, 1612, 1658, 3200, and 3325 cm^{-1}.

Compounds VIIIb-*l* (as colorless or yellow crystals, Table 3) and 4,4'-bis(β-N-vinyldioxolanyl)-aminodiphenyl, with mp 220° (dec.) (in 70% yield), were similarly obtained. Found: C 52.4; H 5.7; Cl 10.0%. $C_{30}H_{38}Cl_2N_2O_{12}$. Calculated: C 52.3; H 5.5; Cl 10.3%.

p-Methoxyanil-2-formylmethylene-4,4,5,5-tetramethyl-1,3-dioxolane (X). A 0.38-g (0.001 mole) sample of VIIIa was shaken with 5 ml of 5% NaOH solution and 10 ml of ether. The ether layer was separated and dried with anhydrous Na_2SO_4. The ether was removed by distillation to give 0.27 g of X (in quantitative yield) as colorless plates with mp 97° (from petroleum ether). IR spectrum: 1140, 1240, 1378, 1460, 1500, 1588, 1608, 1642 cm^{-1}. Found: C 69.4; H 7.7%. $C_{16}H_{21}NO_3$. Calculated: C 69.8; H 7.6%.

2-(β-Ureidovinyl)-4,4,5,5-tetramethyldioxolanium Perchlorate. A 0.3-g (0.005 mole) sample of urea was added to a solution of 1.5 g (0.005 mole) of IIIa in acetic acid, and the mixture was heated until a transparent solution had formed. It was then cooled and diluted with ether, and the resulting oil was allowed to stand overnight. The mixture was filtered to give 1.01 g (65%) of product. The product was crystallized from a small amount of acetic acid to give yellow needles with mp 158-160°. IR spectrum: 1100, 1380, 1570, 1600, 1627, 1750, 3435 cm^{-1}. Found: C 38.0; H 5.4; Cl 11.1%. $C_{10}H_{17}ClN_2O_7$. Calculated: C 38.4; H 5.4; Cl 11.4%.

2-(2-Acetoxy-2-ethoxyethylene)-4,4,5,5-tetramethyl-1,3-dioxolane (XI). A solution of 0.5 ml (0.005 mole) of diethylamine in 3 ml of acetic acid was added to a solution of 0.75 g (0.0025 mole) of IIIa in 5 ml of acetic acid. The mixture was diluted with ether, and the precipitated colorless needles were removed by filtration. The yield of diethylamine perchlorate with mp 155° was 0.43 g (100%). The filtrate was poured into 5% NaOH solution, and the mixture was extracted with ether. The ether was evaporated to give 0.62 g (96%) of a viscous syrup. IR spectrum: 1140, 1250, 1380, 1462, 1630, 1720 cm^{-1}. Found: C 60.6; H 8.9%. $C_{13}H_{22}O_5$. Calculated: C 60.4; H 8.5%.

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