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SYNTHESIS AND PROPERTIES OF HETEROCYCLIC CARBONIUM SYSTEMS.

V.* SYNTHESIS AND REACTIONS OF SOME CYANINES BASED ON DIOXOLANIUM SALTS

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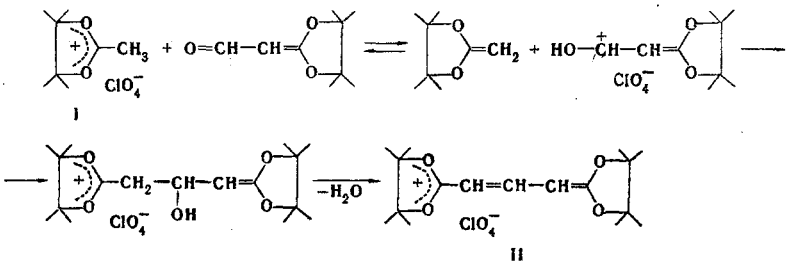
UDC 547.729.7.07

Bis(4,4,5,5-tetramethyl-2-dioxolano)trimethylidynecyanine was synthesized by condensation of 2-methyl-1,3-dioxolanium perchlorate with 2-formylmethylene-1,3-dioxolane by heating (90-100°C) in acetic anhydride. It is shown that the 1,3-dioxolane also condenses under similar conditions with pyrylium salts containing active methylene and methyl groups to give unsymmetrical dioxolanopyrylocyanines. The synthesized cyanines react with $HClO_4$ to give unstable diperchlorates, which readily lose a molecule of $HClO_4$ to give the starting cyanines. Concentrated HCl decomposes one of the dioxolane rings of the symmetrical cyanine, and refluxing with dilute HCl brings about its destruction to low-molecular-weight unidentified compounds. The unsymmetrical cyanine from the pyrylium salt is resistant to the action of acids but is hydrolyzed by alkalis with cleavage of the pyrylium ring to a diketone. The action of Br_2 on the dioxolanocyanine leads to the addition of bromine to the double bonds and replacement of the ClO_4^- ion by Br^-.

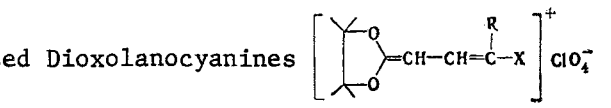
Until now, cyanine dyes that contain a dioxolanium cation were unknown. Our attempt to synthesize a dioxolanocyanine by the traditional method from 2-methyl-1,3-dioxolanium perchlorate (I) and ethyl orthoformate led only to a 2-(β-ethoxyvinyl)-1,3-dioxolanium salt [2], which does not undergo further reaction with starting I. An increase in the temperature and the heating time leads to decomposition of the extremely labile dioxolanium cation. We were able to synthesize dioxolanocyanine II only by condensation of I with 2-formylmethylene-1,3-dioxolane obtained from the 2-(β-ethoxy)vinyl derivative by the action of alkali [2]. The reaction proceeds when the components are heated moderately (90-100°C) in acetic anhydride until they dissolve completely.

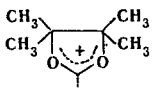
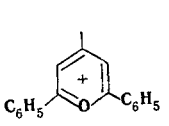
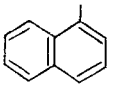
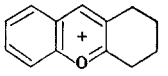
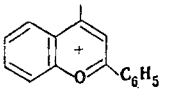


Under similar conditions, 2-formylmethylene-1,3-dioxolane also condenses with pyrylium salts containing active methyl or methylene groups to give unsymmetrical dioxolanopyrylocyanines (Table 1). 2-Methyl-4,6-diphenylpyrylium perchlorate and pyridinium, quinolinium, and

*See [1] for communication IV.

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don 344711. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 5, pp. 595-598, May, 1977. Original article submitted May 14, 1976.

TABLE 1. Synthesized Dioxolanocyanines 

Compound	X	R	mp, °C*	Found, %			Empirical formula	Calc. %			Yield, %
				C	H	Cl		C	H	Cl	
II		H	122	51,7	6,9	9,0	$C_{17}H_{27}ClO_8$	51,7	6,9	8,9	96
III		H	148	64,9	5,8	6,8	$C_{27}H_{27}ClO_7$	65,0	5,5	7,1	82
IV		CH_3	119	65,1	5,8	7,6	$C_{28}H_{29}ClO_7$	65,5	5,7	6,9	80
V		C_6H_5	224—225	68,8	5,6	6,2	$C_{33}H_{31}ClO_7$	68,9	5,4	6,2	98
VI			239	70,5	5,8	6,1	$C_{37}H_{33}ClO_7$	71,1	5,3	5,7	97
VII		H	170—171	60,4	5,7	8,6	$C_{22}H_{25}ClO_7$	60,5	5,8	8,1	82
VIII		H	142	62,2	5,1	8,0	$C_{25}H_{25}ClO_7$	62,7	5,2	7,7	52

*Compounds II and V-VII were crystallized from glacial acetic acid; III, IV, VI, and VIII were purified by reprecipitation from acetone by the addition of ether.

TABLE 2. Spectral Characteristics of the Dioxolanocyanines

Compound	λ'_{max} (lg ε), nm	λ''_{max} (lg ε), nm	λ'''_{max} (lg ε), nm	Principal frequencies in the IR spectrum, cm^{-1}
II		285 (3,88)	383 (4,81)	1620, 1585, 1490, 1100
III	310 (3,39)	381 (3,77)	539 (4,53)	1650, 1575, 1500, 1100,
IV	317 (3,56)	378 (3,96)	555 (4,49)	1650, 1630, 1560, 1500, 1270, 1100
V	316 (3,55)	381 (3,81)	551 (4,52)	1640, 1560, 1520, 1500, 1100
VI		381 (3,98)	549 (4,69)	1655, 1570, 1540, 1500, 1245, 1100
VII	308 (3,63)	365 (3,13)	537 (3,96) 575 (3,92)	1620, 1590, 1565, 1500, 1100
VIII		370 (3,89)	555 (4,48)	1615, 1565, 1500, 1215, 1100

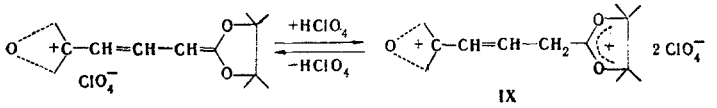
oxazolium salts that have 2-methyl groups do not undergo this reaction even on prolonged refluxing. We were also unable to synthesize mixed cyanines by condensation of pyrylium salts with β-ethoxyvinyldioxolanium perchlorate.

The IR spectrum of symmetrical cyanine II contains absorption bands at 1620 and 1585 cm^{-1}, which can be assigned to the vibrations of conjugated double bonds in the polymethine chain of a cyanine, and the absorption band of the dioxolanium cation at 1490 cm^{-1}. In the spectra of unsymmetrical dioxolanopyrylocyanines III-VIII the absorption bands of the pyrylium cation and the double bonds overlap and appear at 1620-1650 cm^{-1} (Table 2).

The PMR spectrum of compound II contains signals of methyl protons (1.53 ppm, s, 24H) and polymethine-chain protons (d at 5.43 ppm, 2H, and a broad, poorly resolved signal at 8.53 ppm attributed, probably, to the proton at the meso-carbon). The PMR spectrum of unsymmetrical cyanine V also shows a singlet of the protons of four methyl groups of the dioxolanium fragment in the 1.36 ppm region and a multiplet with a center at 7.18 ppm, including the signals of the aromatic and vinyl protons.

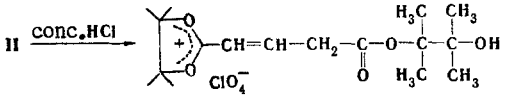
We also studied the absorption spectra of the synthesized cyanine dyes in the visible and ultraviolet regions. The spectrum of dioxolanotrimethylidynecyanine II shows an intense band in the 383 nm region. In the UV spectra of unsymmetrical cyanines containing a pyrylium cation we observed a maximum at 535-555 nm and two less-intense absorption bands in the short-wave region (305-320 and 370-380 nm). In the UV spectra of all the synthesized cyanines, we observed a sharp drop in the long-wave region, characteristic for polymethine dyes (Table 2).

The compounds obtained in this research are protonated when they are treated with perchloric acid to give unstable diperchlorates, which rapidly lose a molecule of $HClO_4$ and are converted to the starting cyanines.



IX

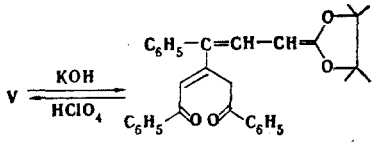
Dilute hydrochloric acid (1:1) readily hydrolyzes dioxolanocyanine II. Only partial decomposition of the molecule to give salt X occurs when it is heated briefly with concentrated hydrochloric acid. Refluxing cyanine II in dilute hydrochloric acid evidently leads to pro-



X

found destruction of the molecule to give water-soluble low-molecular-weight compounds, which we were unable to isolate and identify.

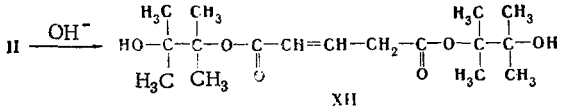
Unsymmetrical cyanine V, which proved to be stable with respect to dilute solutions of mineral acids even on prolonged refluxing, is readily hydrolyzed by alkalis. The attack of the OH^- ion is directed to the pyrylium ring, as a consequence of which the latter is opened to give diketone XI, which on treatment with anhydrous perchloric acid recyclizes to starting cyanine V.



XI

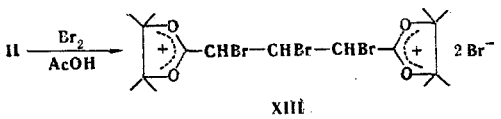
The IR spectrum of XI contains an intense absorption band of a C=O group at 1680 cm^{-1}. We also obtained the same compound in an attempt to replace the heterocyclic oxygen atom by a nitrogen atom by the action of ammonium hydroxide or a solution of ammonium acetate in glacial acetic acid.

Because of delocalization of the positive charge in the symmetrical dioxolanocyanine molecule its reactivity with respect to nucleophilic reagents is considerably lower than in the case of the corresponding dioxolanium salts. It was found that the cyanine is resistant to the action of water, ethanol, and alkali. Perchlorate II is hydrolyzed to an ester only on prolonged treatment with a solution of sodium hydroxide:



XII

Dioxolanocyanine II reacts readily with bromine in glacial acetic acid; in this case, in addition to the addition of bromine to the double bonds, one observes simultaneous replacement of the ClO_4^- ion by Br^-:



XIII

EXPERIMENTAL

The IR spectra of mineral oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of $0.5 \cdot 10^{-4}$-$0.25 \cdot 10^{-4}$ mole/liter chloroform solutions of the compounds were recorded with an SF-16 spectrophotometer. The PMR spectra of salts II (in

nitrobenzene) and V (in trifluoroacetic acid) were recorded with an RYa-2305 spectrometer with an operating frequency of 60 MHz at 20° with hexamethyldisiloxane as the internal standard.

Bis(4,4,5,5-tetramethyl-2-dioxolano)trimethylidynecyanine Perchlorate (II). An 0.24-g (1 mmole) sample of perchlorate I was added to a solution of 0.19 g (1.1 mmole) of 2-formylmethylene-4,4,5,5-tetramethyl-1,3-dioxolane in 5 ml of freshly distilled acetic anhydride, and the mixture was heated carefully until the components dissolved. The solution was then allowed to stand briefly (10-15 min), after which it was diluted with a small amount of ether, and the precipitated yellow crystals were removed by filtration and washed thoroughly with ether. The yield of cyanine II was 0.38 g (96%).

The characteristics of this dye and unsymmetrical cyanines III-VIII, obtained by a similar method, are presented in Tables 1 and 2.

Propene-1,3-bis-2-(4,4,5,5-tetramethyldioxolanium) Diperchlorate (IX). A previously prepared and cooled mixture of 2 ml of acetic anhydride and 0.67 ml of 70% $HClO_4$ was added to 0.3 g (0.76 mmole) of perchlorate II, and the resulting solution was diluted with ether and worked up to give 0.36 g (quantitative yield) of an oily red substance, which began to crystallize rapidly to give a product with mp 136-137°. Found, %: C 40.9; H 5.8; Cl 14.6. $C_{17}H_{28}Cl_2O_{12}$. Calculated, %: C 41.2; H 5.7; Cl 14.3.

Acid Hydrolysis of Dioxolanocyanine II. A mixture of 0.4 g (1 mmole) of cyanine II and 6 ml of concentrated HCl was heated to the boiling point, during which the starting perchlorate gradually dissolved and a yellowish amorphous precipitate began to form immediately. The precipitate was removed by filtration, washed with water, and dried to give 0.2 g (50%) of salt X with mp 185° (dec. explosively). Found, %: C 49.3; H 7.3; Cl 8.4. $C_{17}H_{29}Cl_9O_9$. Calculated, %: C 49.2; H 7.5; Cl 8.5. IR spectrum: 1720, 1600, 1545, and 1100 cm^{-1}.

Alkaline Hydrolysis of the Dioxolanocyanines. A mixture of 0.4 g (1 mmole) of perchlorate II and 10 ml of 30% KOH solution was allowed to stand at room temperature for 12 h, after which it was extracted with ether. The ether extract was washed with dilute HCl solution and water and dried with Na_2SO_4. The solvent was removed by distillation to give 0.24 g (72%) of the pinacol ester of glutaconic acid (XII). Found, %: C 61.8; H 9.1. $C_{17}H_{30}O_6$. Calculated, %: C 61.8; H 9.1. IR spectrum: 3450, 1730, 1610, 1590, and 1380 cm^{-1}.

Unsymmetrical dioxolanopyrylocyanine V was hydrolyzed for 30 min. The yield of the corresponding diketone XI, with mp 204-205° (purified by chromatography with a column filled with Al_2O_3 and elution with $CHCl_3$), was quantitative. Found, %: C 80.9; H 6.3. $C_{33}H_{32}O_4$. Calculated, %: C 80.5; H 6.5. IR spectrum: 1680, 1575, 1530, 1500, and 1250 cm^{-1}.

1,2,3-Tribromopropane-1,3-bis-2-(4,4,5,5-tetramethyldioxolanium) Dibromide (XIII). An 0.4-g (1 mmole) sample of perchlorate II was dissolved in 10 ml of glacial acetic acid, and bromine was then added dropwise until the resulting coloration no longer disappeared. The yellow-orange crystals that precipitated immediately were removed by filtration and washed with ether. An additional amount of product was obtained by dilution of the mother liquor with ether to give a total of 0.4 g (75%) of XIII with mp 117-118°. Found, %: C 29.3; H 4.2; Br 56.8. $C_{17}H_{27}Br_5O_4$. Calculated, %: C 29.4; H 3.9; Br 57.5. IR spectrum: 1560, 1320, 1290, 1250, and 1170 cm^{-1}.

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