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Acetals and Vinyl Ethers of Unsaturated Aldehydes and Ketones in the New Syntheses of Heterocyclic Compounds: XII.* New Alternatives of Acid Condensation of Cyclohexane-1,4-diones with Hydroxyarylaldehydes under Dehydration Conditions. Fluorecence Spectra of the Products**

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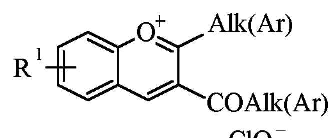
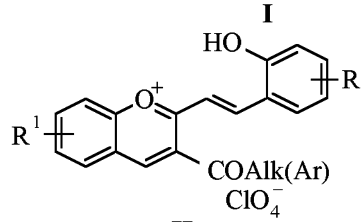
Abstract—1,3-Diethoxy-2-R-5,5-R',R'-1-cyclohexenylium perchlorates in condensation with 2-hydroxyarylaldehydes under dehydration conditions give rise to 3-ethoxy-1,2-dihydroxanthylium perchlorates that with the second molecule of 2-hydroxyarylaldehyde afford 13*H*-chromeno[3,2-b]xanth-5-ylium perchlorates, and with primary and secondary amines yield 3-(R^2,R^3-amino)-1,2-dihydroxanthylium perchlorates. The condensation of 2-bromodimedone with salicylaldehydes in triethyl orthoformate and perchloric acid medium furnished 6-bromo-13,13-dimethyl-13*H*-chromeno[3,2-b]xanth-5-ylium perchlorates. The latter compounds show strong fluorescence in 530–630 nm region with 0.48–0.98 quantum efficiency. Under similar conditions the dimedone and 2-acetyldimedone afford with 2-hydroxyarylaldehydes tris-condensation products: 2,10-dimethoxy-6-(3-methoxy-6-oxo-2,4-cyclohexadienylidenemethyl)-7,7-dimethyl-7*H*-chromeno[2,3-a]-xanth-13-ylium perchlorate and 2,10-dimethoxy-6-(6-methoxychromylium-2-yl)-13,13-dimethyl-13H-chromeno[3,2-b]xanth-5-ylium diperchlorate respectively.

The condensation of 1,3-diketones and 2-hydroxyarylaldehydes under treatment with perchloric acid is known to occur at the central carbon atom of the carbon triad of the diketone yielding 2-hydroxystyryl derivatives that cyclize further into benzpyrylium salts **I** [2]. With 1,3-diketones possessing terminal methyl groups (acetylacetone, benzoylacetone) the condensation affords 3-acetyl(benzoyl)-2-(2-hydroxystyryl)-1-benzopyrylium perchlorate (**II**) [3, 4]. Oxoenols containing a methyl group in *1* position (benzoylacetone, pivaloylacetone) with triethyl orthoformate and perchloric acid give rise to 2-R-4-ethoxypyrylium perchlorates **III** [5]. Under such conditions from dimedone and dibenzoylmethane were obtained stable perchlorates of 5,5-dimethyl-1,3-diethoxy-1-cyclohexenylium (**IVa**) and 1,3-diphenyl-1,3-diethoxypropenylium (**V**) respectively [6] that could operate as synthons in preparation of cyclic and acyclic oxoenols derivatives by replacement of the ethoxy groups [7].

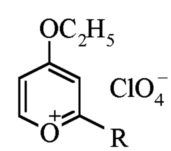
Thus in reaction of oxoenols with more basic 2-hydroxyarylaldehydes [8] the reactive form is the protonated aldehyde function, and the condensation occurs at the central atom of the oxoenol carbon triad. On the contrary, in reaction with triethyl orthoformate the 1,3-diketone is more basic, and it is



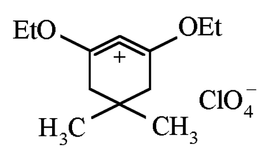
I



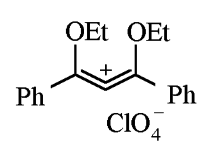
II



III



IVa



V

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* For communication XI, see [1].

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stabilized on protonation as 1,3-dihydroxypropenylium cation. Therefrom it may be concluded that the choice of reagents and condensation conditions for the reaction with 2-hydroxyarylaldehydes may result in compounds with important physico-chemical characteristics unlike the products of Knoevenagel condensation [9].

In the study were used 1,3-diethoxy-2-R-5,5-R',R'-1-cyclohexenylium perchlorates, unsubstituted and 2-substituted 5,5-dimethylcyclohexane-1,3-dione, dehydrating reagents (triethyl orthoformate, acetic anhydride), 70% perchloric acid, 16% solution of perchloric acid in acetic acid, and various 2-hydroxyarylaldehydes. Since a propenyl cation of **IV** type derived from dimedone has two activated methylene groups in *4* and *6* positions it seemed promising to use it in condensation with hydroxyarylaldehydes. To this end were studied the previously described perchlorate **IVa** [6], and also first obtained perchlorates of 2-bromo-5,5-dimethyl-1,3-diethoxycyclohexenylium (**IVb**) and 1,3-diethoxy-1-cyclohexenylium (**IVc**).

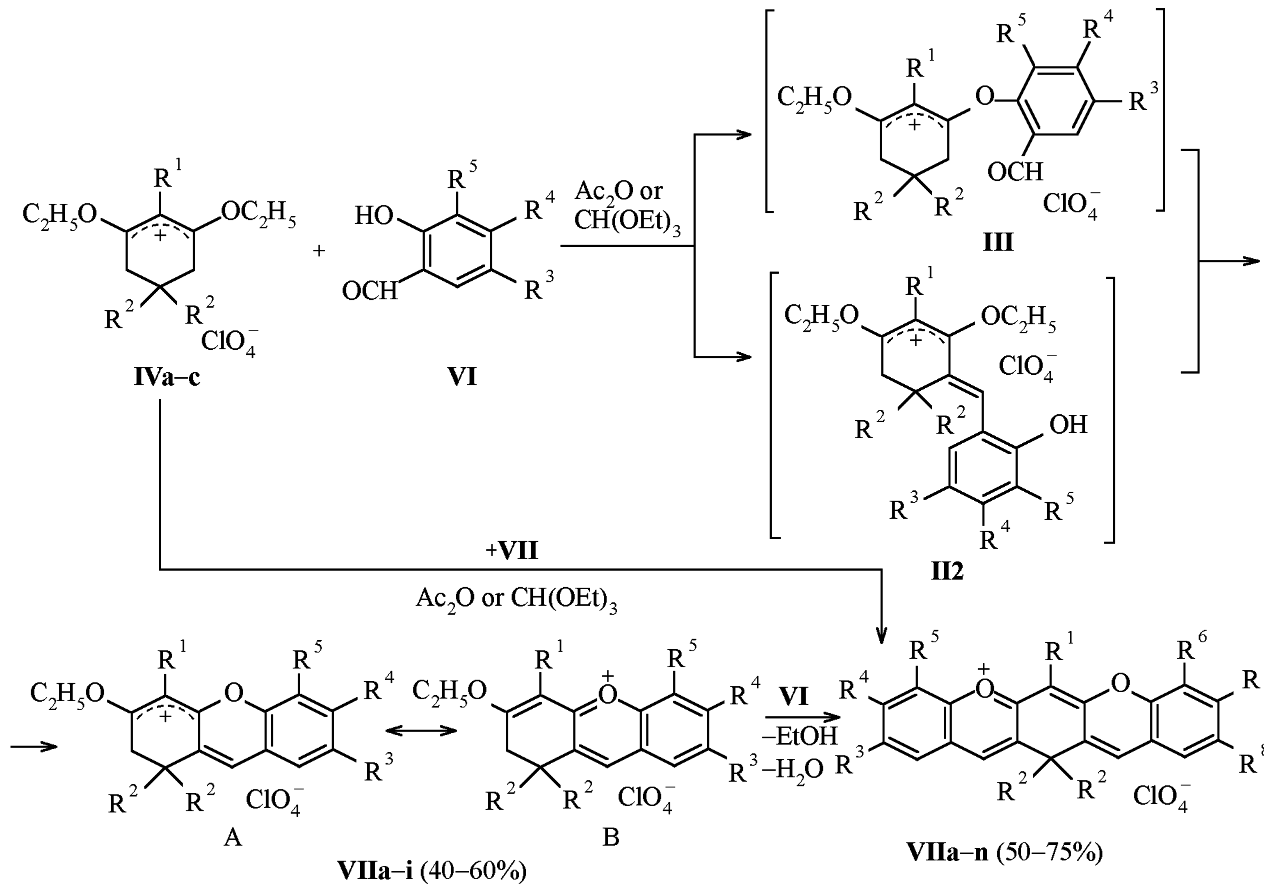
At equimolar ratio of 2-hydroxyarylaldehydes **VI** with 1,3-diethoxy-2-R-5,5-R',R'-1-cyclohexenylium perchlorates **IVa–c** under dehydrating conditions (triethyl orthoformate, acetic anhydride) the condensation furnished perchlorates of substituted 3-ethoxy-1,2-dihydroxanthylium **VIIa–i**. Salts **VII** can form along two alternative routes: the first path starts with replacement of the ethoxy group by phenoxy one (P1) with subsequent condensation; along the second path occurs the condensation of a formyl group (P2) followed by transetherification. The first path is presumably more probable since as has been stated in [1] perchlorate **IVa** does not react with anisaldehyde apparently because of steric hindrance from the methyl groups in position *5*. The condensation of perchlorates **IVa, b** with two moles of 2-hydroxyarylaldehyde **VI**, or of salts **VIIa–i** with one mole of aldehyde **VI** results in 13H-chromeno[3,2-b]xanth-5-ylium perchlorates **VIIIa–n** (Scheme 1). Certain perchlorates of **VIII** type were prepared before [10] and were used as luminescent dyes photoactive in the region 600–650 nm. For instance, salts **VIII** were prepared from dimedone sodium salts, its 2-alkyl derivatives, butyllithium, and sodium salts of 2-hydroxyarylaldehydes with subsequent hydrolysis and treatment with perchloric acid, and the yields did not exceed 16%. Unlike that our procedure permits application of 2-halosubstituted dimedones and provides also nonsymmetrical salts **VIIId–f** in 50–75% yield.

In the IR spectra of perchlorates **VIIa–i** are present absorption bands in the region 1570–1590, 1200–1250, 1050–1150 cm^{-1} characteristic of the bonds C=C, C–O–C, and ClO respectively [11]. The data on yields, melting points, and composition of compounds **VIIa–i** are given in Table 3, parameters of IR and ^{1}H NMR spectra in Table 5. Electron absorption spectra of compounds **VIIb–h** in acetonitrile solution contain two bands in the longwave region with pronounced vibronic structure: two strong [ε $(2.5–6.0)\times 10^4$ $l\,mol^{-1}\,cm^{-1}$] bands with maxima λ^{abs}_{1max} and λ^{abs}_{2max} in the region 494–532 and 527–558 nm respectively (Table 1). Electron-donor substituents (R^3 = Br, CH_3O) provide a shift of the maxima λ^{abs}_{1max} and λ^{abs}_{2max} to the longwave region with respect to those in the unsubstituted compound **VIIb** (R^1 = H), and electron-acceptor group (R^3 = NO_2) effects a shift to the shortwave region. The acetonitrile solutions of perchlorates **VIIa–h** show strong fluorescence with the quantum efficiency φ 0.73–0.98 (Table 1). The fluorescence spectra of compounds **VIIb–h** solutions are wide bands with two maxima λ^{fl}_{1max} and λ^{fl}_{2max}, whereas the short-wave maximum (λ^{fl}_{1max}) is stronger than that in the longwave region (λ^{fl}_{2max}). The latter maximum in the spectrum of compound **VIIc** appears as a shoulder. The maxima of the fluorescent bands are located in the regions 532–570 and 570–620 nm respectively. The position of the bands in the fluorescence excitation spectra is the same as the maxima in the corresponding electron absorption spectra. The electron-acceptor characteristics of the R^3 substituent affect the fluorescent spectra similarly to the effect on the electron absorption spectra discussed above.

Physical constants, yields, and elemental analyses of perchlorates **VIII** are given in Table 4, the spectral characteristics are presented in Table 6. In the electron absorption spectra of compounds **VIIIa–j**, of their bromoderivatives **VIIIk–v** appear as in the respective spectra of compounds **VIIa–h** absorption bands in the longwave region with two maxima λ^{abs}_{1max} and λ^{abs}_{2max}.

The electron-donor properties of the R^1 = Br substituent appear as red shift of the absorption maxima in the brominated compounds with respect to nonbrominated **VIIIa–j** compounds (R^1 = H) (e.g. comparing compounds **VIIIb** with **VIIIk, VIIIc** with **VIIIn**) (Table 2). In each series **VIIIa–j** and **VIIIk–v** the effect of electronic properties of substituents R^3–R^8 on the absorption spectra is similar to that observed in the spectra of compounds **VII**: the

Scheme 1.



VII, $R^1 = R^2 = R^4 = R^5 =$ H, $R^3 = CH_3O$ (**a**); $R^2 = CH_3$, $R^1 = R^5 =$ H (**b**); $R^2 = CH_3$, $R^3 = CH_3O$, $R^1 = R^4 = R^5 =$ H (**c**); $R^2 = CH_3$, $R^1 = R^3 = R^4 =$ H, $R^5 = CH_2CH{=}CH_2$ (**d**); $R^2 = CH_3$, $R^3 =$ Br, $R^1 = R^4 = R^5 =$ H (**e**); $R^2 = CH_3$, $R^3 = NO_2$, $R^1 = R^4 = R^5 =$ H (**f**); $R^2 = R^4 = R^5 = R^6 = R^7$, $R^3 = CH_3$, $R^1 = R^4 = R^5 =$ H (**g**); $R^1 =$ Br, $R^2 = CH_3$, $R^3 = R^4 = R^5 =$ H (**h**); $R^1 =$ Br, $R^2 = CH_3$, $R^3 = CH_3O$, $R^4 = R^5 =$ H (**i**); **VIII**, $R^1 = R^2 =$ H, $R^4 = R^5 = R^6 = R^7 =$ H, $R^3 = R^8 = CH_3O$ (**a**); $R^1 =$ H, $R^2 = CH_3$, $R^3 = R^4 = R^5 = R^6 = R^7 = R^8 =$ H (**b**); $R^2 = CH_3$, $R^1 =$ H, $R^3 = R^8 = CH_3O$, $R^4 = R^5 = R^6 = R^7 =$ H (**c**); $R^2 = CH_3$, $R^1 =$ H, $R^3 = CH_3O$, $R^8 = NO_2$, $R^4 = R^5 = R^6 = R^7 =$ H (**d**); $R^2 = CH_3$, $R^1 =$ H, $R^3 = CH_3O$, $R^8 =$ Br, $R^4 = R^5 = R^6 = R^7 =$ H (**e**); $R^2 = CH_3$, $R^1 =$ H, $R^3 = CH_3O$, $R^4 = R^5 = R^6 = R^7 = R^8 =$ H (**f**); $R^2 = CH_3$, $R^1 =$ H, $R^3 = CH_3O$, $R^6 = CH_2CH{=}CH_2$ (**g**); $R^2 = CH_3$, $R^1 =$ H, $R^3 = CH_3O$, $R^7 =$ OH, $R^4 = R^5 = R^6 =$ H, $R^8 =$ H (**h**); $R^2 = CH_3$, $R^1 =$ H, $R^3 = R^8 = CH_3O$, $R^6 = NO_2$, $R^4 = R^5 =$ H, $R^7 =$ H (**i**); $R^2 = CH_3$, $R^1 =$ H, $R^3 = CH_3O$, $R^4 = R^5 =$ H, $R^6 = R^8 =$ Cl, $R^7 =$ H (**j**); $R^2 = CH_3$, $R^1 =$ Br, $R^3 = R^4 = R^5 = R^6 = R^7 = R^8 =$ H (**k**); $R^2 = CH_3$, $R^1 =$ Br, $R^3 = R^8 = CH_3$, $R^4 = R^5 = R^6 = R^7 =$ H (**l**); $R^2 = CH_3$, $R^1 =$ Br, $R^4 = R^7 = CH_3$, $R^3 = R^5 = R^6 = R^8 =$ H (**m**); $R^2 = CH_3$, $R^1 =$ Br, $R^3 = R^8 = CH_3O$, $R^4 = R^5 = R^6 = R^7 =$ H (**n**).

electron-acceptor groups produce blue shift of the maxima of the longwave band, the electron-donor groups produce red shift. Note that perchlorate **VIIIu**, [$R^3 = R^8 = N(CH_3)_2$], has a single longwave maximum in acetonitrile solution at 698 nm. The acetonitrile solutions of compounds **VIIIa–j** and **VIIIk–v** show fluorescence with quantum efficiency 0.54–0.96 and 0.48–0.87 respectively (Table 2). The maxima of the fluorescence bands of perchlorates **VIIIa–j** are located in the region λ^{fl}_{1max} 537–590 and λ^{fl}_{2max} 570–630 nm.

The maxima of the fluorescence bands of the salts **VIIIk–v** are somewhat shifted to more longwave region: λ^{fl}_{1max} 558–590 and λ^{fl}_{2max} 595–634 nm. Therewith the fluorescence band of compound **VIIIu** [$R^3 = R^8 = N(CH_3)_2$] has a single maximum at 715 nm. The quantum efficiencies of fluorescence for

Table 1. Electron absorption spectra and fluorescence spectra of derivatives of 1,2-dihydroxanthylium **VIIb**–**e; IXa**–**k; Xa**–**e,** and **XIIb** in acetonitrile solution

No.	Absorption		Fluorescence	
	λ_{max}, nm	$\varepsilon \times 10^3$, $l\,mol^{-1}\,cm^{-1}$	λ_{max}, nm	φ[a]
VIIb	498	44.86	536	0.96
	532	60.87	580	
VIIc	521	38.75	570	0.73
	558	59.20	620 fl	
VIIe	502	37.50	552	0.98
	537	52.61	590	
VIIf	494	39.02	543	0.87
	527	53.28	590	
VIIg	514	26.5	532	0.80
	544	49.6	570	
IXa	521	65.74	570	0.82
	558	100.27	620	
IXb	521	61.69	570	0.86
	557	94.47	620	
IXc	521	77.68	570	0.84
	558	118.14	620 fl	
IXd	527	62.28	570	0.82
	558	95.07	620 fl	
IXe	521	81.42	570	0.81
	558	123.04	620	
IXf	521	55.06	570	0.88
	558	78.97	620	
IXg	521	56.17	570	0.92
	558	83.24	620	
IXh	521	46.10	570	0.83
	558	66.63	620	
IXi	498	60.33	537	0.88
	532	73.33	580	
IXj	521	22.08	570	0.77
	558	33.87	620	
Xa	521	3.80	570	0.89
	558	5.45	620	
Xb	521	3.60	570	0.89
	558	4.90	620	
Xc	521	3.42	570	0.62
	558	3.50	620	
Xd	521	6.35	570	0.84
	558	9.16	620	
XIIb	521	9.62	570	0.86
	558	17.25	620	

[a] Quantum efficiency of fluorescence.

Table 2. Electron absorption spectra and fluorescence spectra of perchlorates of 13*H*-chromeno[3,2-*b*]xanth-5-ylium (**VIIIa**–**v**) in acetonitrile solution

No.	Absorption		Fluorescence	
	λ_{max}, nm	$\varepsilon \times 10^3$, $l\,mol^{-1}\,cm^{-1}$	λ_{max}, nm	φ[a]
VIIIa	528	31.33	580	0.51
	562	36.56		
VIIIb	498	69.70	537	0.96
	532	85.56	570	
VIIIc	521	51.75	570	0.70
	558	74.34	620	
VIIId	521	57.57	570	0.74
	559	81.81	620	
VIIIe	502	49.36	543	0.72
	539	64.70	588	
VIIIf	534	54.68	588	0.78
	573	84.34	630	
VIIIg	521	58.50	570	0.74
	558	83.88	620	
VIIIh	534	37.22	590	0.54
	573	62.91	625 fl	
VIIIi	521	46.03	570	0.67
	558	63.25	620	
VIIIj	521	69.28	570	0.76
	561	96.87	620	
VIIIk	512	22.59	560	0.48
	548	33.54	595 fl	
VIIIl	519	53.12	570	0.82
	556	82.80	620	
VIIIm	525	25.00	573	0.69
	563	40.16	620	
VIIIn	532	56.03	590	0.53
	573	85.65	634	
VlIIo	510	36.26	558	0.61
	548	57.69	628	
VIIIp	519	27.76	570	0.65
	558	45.02	618	
VIIIq	517	71.00	565	0.75
	556	102.25	620	
VIIIr	514	59.15	564	0.78
	553	87.73	605 fl	
VIIIs	514	66.77	560	0.85
	551	105.16	600 fl	
VIIIt	514	60.73	565	0.87
	553	90.38	620	
VIIIu	698	81.79	715	–
VIIIv	532	66.23	570	0.66
	573	113.76	620	

[a] Quantum efficiency of fluorescence.

Table 3. Yields, melting points, and elemental analyses of derivatives of 1,2-dihyroxanthylium **VIIb**–**i, IXa**–**j, Xa**–**d, XIa**–**d, XIIa,b**

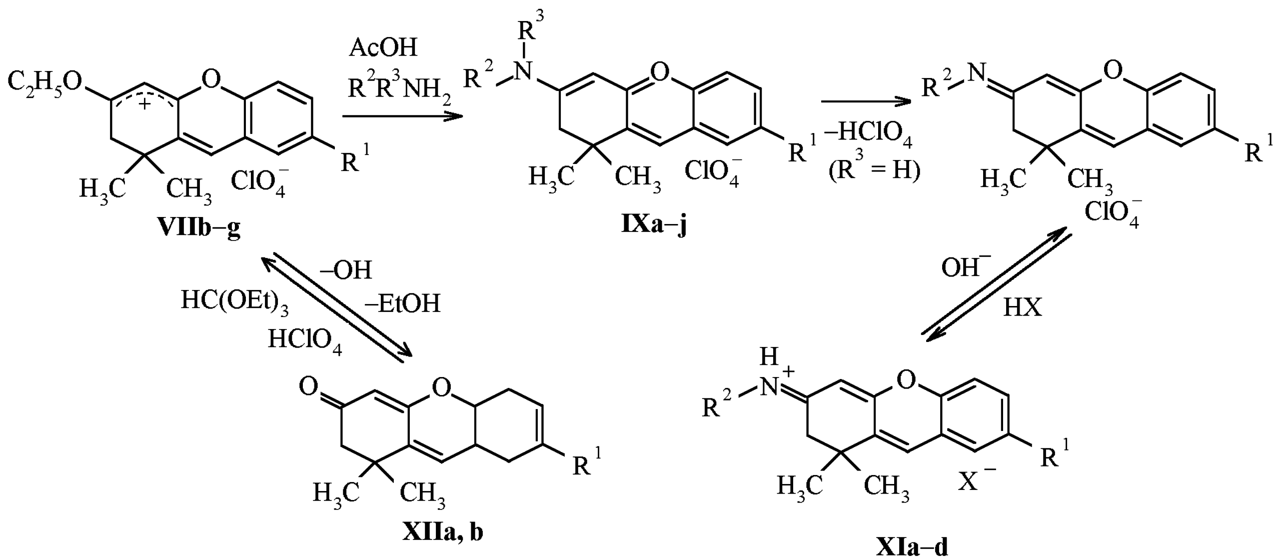
Compd. no.	Yield, %	mp, °C	Found, %				Formula	Calculated, %			
			C	H	Hlg	N		C	H	Hlg	N
VIIb	62	207–210	57.59	5.36	10.68	–	$C_{17}H_{19}ClO_6$	57.55	5.40	9.99	–
VIIc	70	194–195	56.11	5.43	9.30	–	$C_{18}H_{21}ClO_7$	56.18	5.50	9.21	–
VIId	57	108–110	60.75	5.81	9.06	–	$C_{20}H_{23}ClO_6$	60.84	5.87	8.98	–
VIIe	64	238–240	47.01	3.96	26.95	–	$C_{17}H_{18}BrClO_6$	47.08	4.18	26.60	–
VIIf	74	247–249	50.57	4.36	8.98	3.64	$C_{17}H_{18}ClNO_8$	51.07	4.45	8.87	3.50
VIIg	65	201–203	58.5	5.70	9.75	–	$C_{18}H_{21}ClO_6$	58.62	5.74	9.61	–
VIIh	69	184–186	47.02	4.25	26.68	–	$C_{17}H_{18}BrClO_6$	47.08	4.18	26.60	–
VIIi	73	192–193	46.51	4.39	24.92	–	$C_{18}H_{20}BrClO_7$	46.62	4.35	24.88	–
IXa	78	208–209	61.01	5.04	8.35	3.36	$C_{22}H_{22}ClNO_6$	61.18	5.14	8.21	3.24
IXb	74	221–222	51.70	4.22	22.67	2.60	$C_{22}H_{21}BrClNO_6$	51.73	4.15	22.59	2.74
IXc	76	210–213	61.63	5.32	8.21	3.25	$C_{23}H_{24}ClNO_6$	61.95	5.43	7.95	3.14
IXd	71	197–199	59.70	5.14	7.86	3.22	$C_{23}H_{24}ClNO_7$	59.81	5.24	7.68	3.03
IXe	52	246–248	57.65	4.40	7.68	2.99	$C_{23}H_{22}ClNO_8$	58.05	4.66	7.45	2.94
IXf	46	230–232	59.43	5.07	7.25	2.93	$C_{25}H_{26}ClNO_8$	59.58	5.20	7.04	2.78
IXg	54	276–277	59.44	5.14	7.15	2.91	$C_{25}H_{26}ClNO_8$	59.58	5.20	7.04	2.78
IXh	68	244–245	61.82	5.32	8.03	3.22	$C_{23}H_{24}ClNO_6$	61.95	5.43	7.95	3.14
IXi	68	271–273	58.21	6.31	8.75	3.47	$C_{20}H_{26}ClNO_6$	58.32	6.36	8.61	3.40
IXj	59	206–207	56.18	5.51	8.49	3.52	$C_{20}H_{24}ClNO_7$	56.40	5.68	8.33	3.29
Xa	91	179–180	79.60	6.32	–	4.30	$C_{22}H_{21}NO_2$	79.73	6.39	–	4.23
Xb	94	153–154	79.82	6.60	–	4.15	$C_{23}H_{23}NO_2$	79.97	6.71	–	4.06
Xc	81	129–130	76.29	6.35	–	3.99	$C_{23}H_{23}NO_3$	76.43	6.41	–	3.88
Xd	89	152–153	64.28	4.79	19.59	3.50	$C_{22}H_{20}BrNO_2$	64.40	4.91	19.48	3.41
XIa	90	201–203	64.01	5.29	19.49	3.48	$C_{22}H_{22}BrNO_2$	64.08	5.38	19.38	3.40
XIb	92	208–210	64.68	5.60	18.85	3.35	$C_{23}H_{24}BrNO_2$	64.79	5.67	18.74	3.29
XIc	85	195–196	62.36	5.39	18.19	3.26	$C_{23}H_{24}crNO_3$	62.45	5.47	18.07	3.17
XId	92	214–215	53.68	4.23	32.64	2.93	$C_{22}H_{21}Br_2NO_2$	53.79	4.31	32.54	2.85
XIIa	91	181–183	79.50	6.21	–	–	$C_{15}H_{14}O_2$	79.62	6.24	–	–
XIIb	95	136–137	74.85	6.22	–	–	$C_{16}H_{16}O_3$	74.98	6.29	–	–

perchlorates **VIIIk–v** solutions have lower values than for salts **VIIIa–j** apparently due to the presence in the former of bromine atoms: The heavy atoms are known to increase the velocity of intercombination conversion $S_1 \rightarrow T_1$ that reduces the efficiency of the fluorescence [12].

It is presumable that salts **VIIa–i** in the resonance form **VIIA** the charge is localized mostly on the unsaturated ring of the molecule for they readily exchange the activated ethoxy group with amino-containing nucleophiles to afford 3-(R^2,R^3-amino)-1,2-dihydroxanthylium perchlorates **IXa–k**. On treating perchlorates **IXa–g** with bases (sodium acetate) were obtained (1*H*-2,3-dihydroxanthen-3-ylidene)-(R^2-phenyl)amines **XIa–d**. Perchlorates **VII** in aqueous basic medium readily undergo hydrolysis yielding 1*H*-2,3-dihydroxanthen-3-ones (**XIIa, b**) (Scheme 2).

In the IR spectra of perchlorates and bromides of 3-(R^2,R^3-amino)-1,2-dihydroxanthylium **IXa–g** and **XIa–d** should be noted the absorption bands at 3260–3280 cm^{-1} characteristic of NH group, and by xanthenones **XIIa, b** is noteworthy the absorption band in the 1685–1700 cm^{-1} region belonging to carbonyl group C=O [11]. In the ^{1}H NMR spectra of perchlorates **IXa–g** the proton signal from $=N^+HAr$ group at 7.60–7.80 ppm evidences the prevailing contribution from the immonium resonance

Scheme 2.

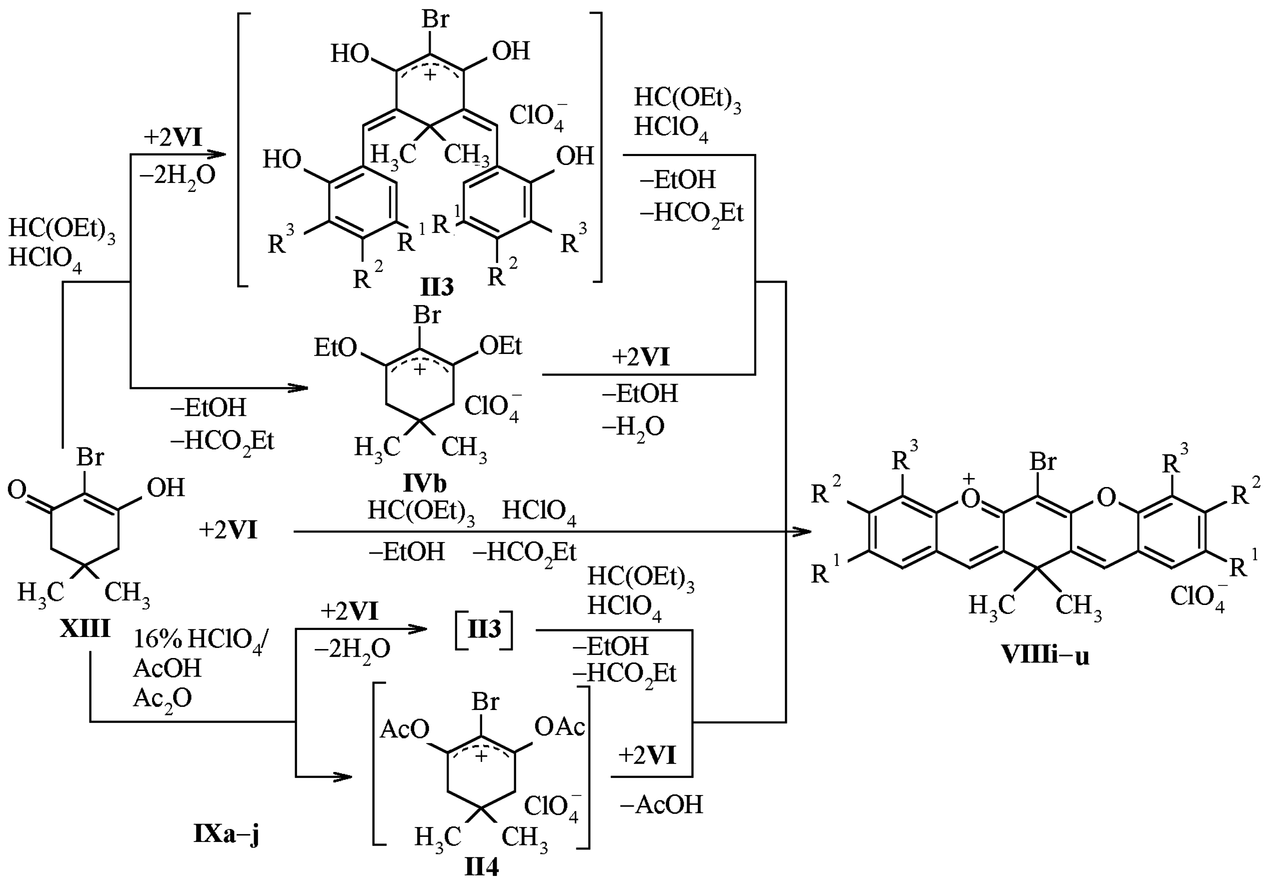


IX, R^1 = CH_3O, R^2 = C_6H_5, R^3 = H (**a**); R^1 = CH_3O, R^2 = 4-BrC_6H_4, R^3 = H (**b**); R^1 = CH_3O, R^2 = 4-$CH_3C_6H_4$, R^3 = H (**c**); R^1 = = CH_3O, R^2 = 4-$CH_3OC_6H_4$, R^3 = H (**d**); R^1 = CH_3O, R^2 = 4-$HOOCC_6H_4$, R^3 = H (**e**); R^1 = CH_3O, R^2 = 4-$C_2H_5COOC_6H_4$, R^3 = H (**f**); R^1 = CH_3O, R^2 = 2-$C_2H_5COOC_6H_4$, R^3 = H (**g**); R^1 = CH_3O, R^2 = C_6H_5, R^3 = CH_3 (**h**); R^1 = CH_3O, R^2 = R^3 = C_2H_5 (**i**); R^1 = CH_3O, R^2 = R^3 = $(CH_2)_2O(CH_2)_2$ (**j**); **X**, R^1 = CH_3O, R^2 = C_6H_5 (**a**); R^1 = CH_3O, R^2 = 4-$CH_3C_6H_4$ (**b**); R^1 = CH_3O, R^2 = 4-$CH_3OC_6H_4$ (**c**); R^1 = CH_3O, R^2 = 4-BrC_6H_4 (**d**); **XI**, R^1 = CH_3O, R^2 = C_6H_5 (**a**); R^1 = CH_3O, R^2 = 4-$CH_3C_6H_4$ (**b**); R^1 = CH_3O, R^2 = 4-$CH_3OC_6H_4$ (**c**); R^1 = CH_3O, R^2 = 4-BrC_6H_4 (**d**); **XII**, R^1 = H (**a**); CH_3O (**b**).

Table 4. Yields, melting points, and elemental analyses of 13*H*-chromeno[3,2-**b**]xanth-5-ylium perchlorates **VIIIa**–**v**

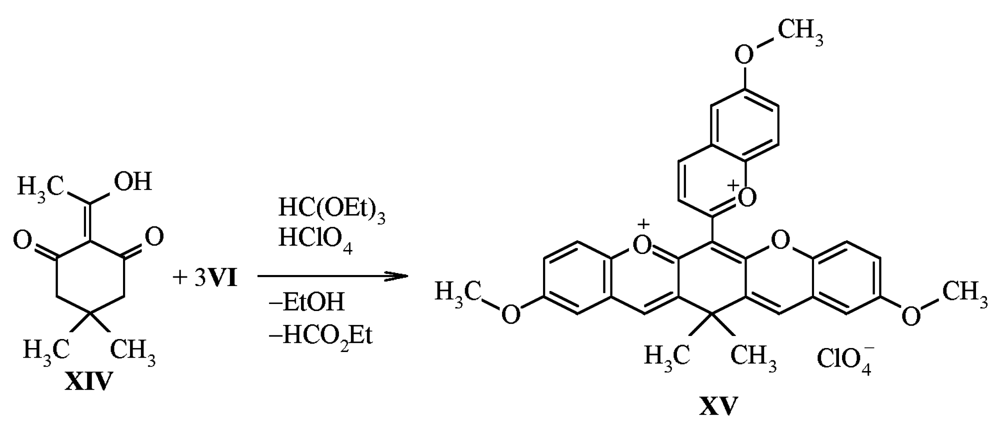
Compd. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	Hlg (N)		C	H	Hlg (N)
VIIIb	55	294–297	63.86	4.03	8.71	$C_{22}H_{17}ClO_6$	64.01	4.15	8.59
VIIIc	59	303–305	60.91	4.40	7.64	$C_{24}H_{21}ClO_8$	60.96	4.48	7.50
VIIId	54	314–315	56.51	3.65	7.39 (2.5)	$C_{23}H_{18}ClNO_9$	56.62	3.72	7.27 (2.87)
VIIIe	63	355–358	52.90	3.55	22.17	$C_{23}H_{18}ClBrO_7$	52.95	3.48	22.11
VIIIf	55	291–292	62.31	4.36	8.05	$C_{23}H_{19}ClO_7$	62.38	4.32	8.01
VIIIg	48	247–249	64.60	4.72	7.44	$C_{26}H_{23}ClO_7$	64.66	4.80	7.34
VIIIh	58	312–314	60.16	4.11	7.86	$C_{23}H_{19}ClO_8$	60.20	4.17	7.73
VIIIi	52	301–303	55.69	3.74	6.78 (2.67)	$C_{24}H_{20}ClNO_{10}$	55.66	3.89	6.85 (2.71)
VIIIj	57	296–297	53.95	3.31	20.85	$C_{23}H_{17}Cl_3O_7$	53.98	3.35	20.79
VIIIk	55	308–310	33.12	3.23	23.51	$C_{22}H_{16}crClO_6$	33.47	3.28	23.46
VIIIl	44	305–307	55.41	3.84	22.07	$C_{24}H_{20}crClO_6$	55.46	3.88	22.19
VIIIm	41	303–305	55.42	3.94	22.12	$C_{24}H_{20}crClO_6$	55.46	3.88	22.19
VIIIn	54	307–309	52.30	3.85	19.92	$C_{24}H_{20}crClO_8$	52.24	3.65	20.91
VIIIo	55	342–344	45.58	2.36	19.74 (4.72)	$C_{24}H_{14}BrClN_2O_{10}$	45.42	2.42	19.83 (4.80)
VIIIp	69	341–343	32.55	1.72	53.80	$C_{22}H_{12}cr_5ClO_6$	32.73	1.50	53.88
VIIIq	63	301–303	40.91	2.03	42.48	$C_{22}H_{14}cr_3ClO_6$	40.68	2.17	42.56
VIIIr	51	322–324	47.31	2.63	33.07	$C_{22}H_{14}crCl_3O_6$	47.13	2.52	33.23
VIIIs	67	219–220	59.05	4.22	20.07	$C_{28}H_{24}crClO_6$	58.81	4.23	20.17
VIIIt	46	348–350	47.43	2.80	18.75 (4.57)	$C_{24}H_{18}BrClN_2O_6$	47.27	2.97	18.92 (4.60)
VIIIu	41	318–320	54.21	4.45	19.90 (4.87)	$C_{26}H_{26}crClN_2O_6$	54.04	4.54	19.96 (4.85)
VIIIv	43	345–347	33.50	1.74	49.95	$C_{24}H_{16}Br_5ClO_8$	33.23	1.86	50.15

Scheme 3.



VIII, R^1 = NO_2, R^2 = R^3 = H (**n**); R^1 = R^3 = Br, R^2 = H (**o**); R^1 = Br, R^2 = R^3 = H (**p**); R^1 = Cl, R^2 = R^3 = H (**q**); R^1 = R^2 = H, R^3 = $CH_2CH{=}CH_2$ (**r**); R^1 = CH_3, R^2 = NO_2, R^3 = H (**s**); R^1 = R^3 = H, R^2 = $N(CH_3)_2$ (**t**); R^1 = R^3 = Br, R^2 = CH_3O (**u**).

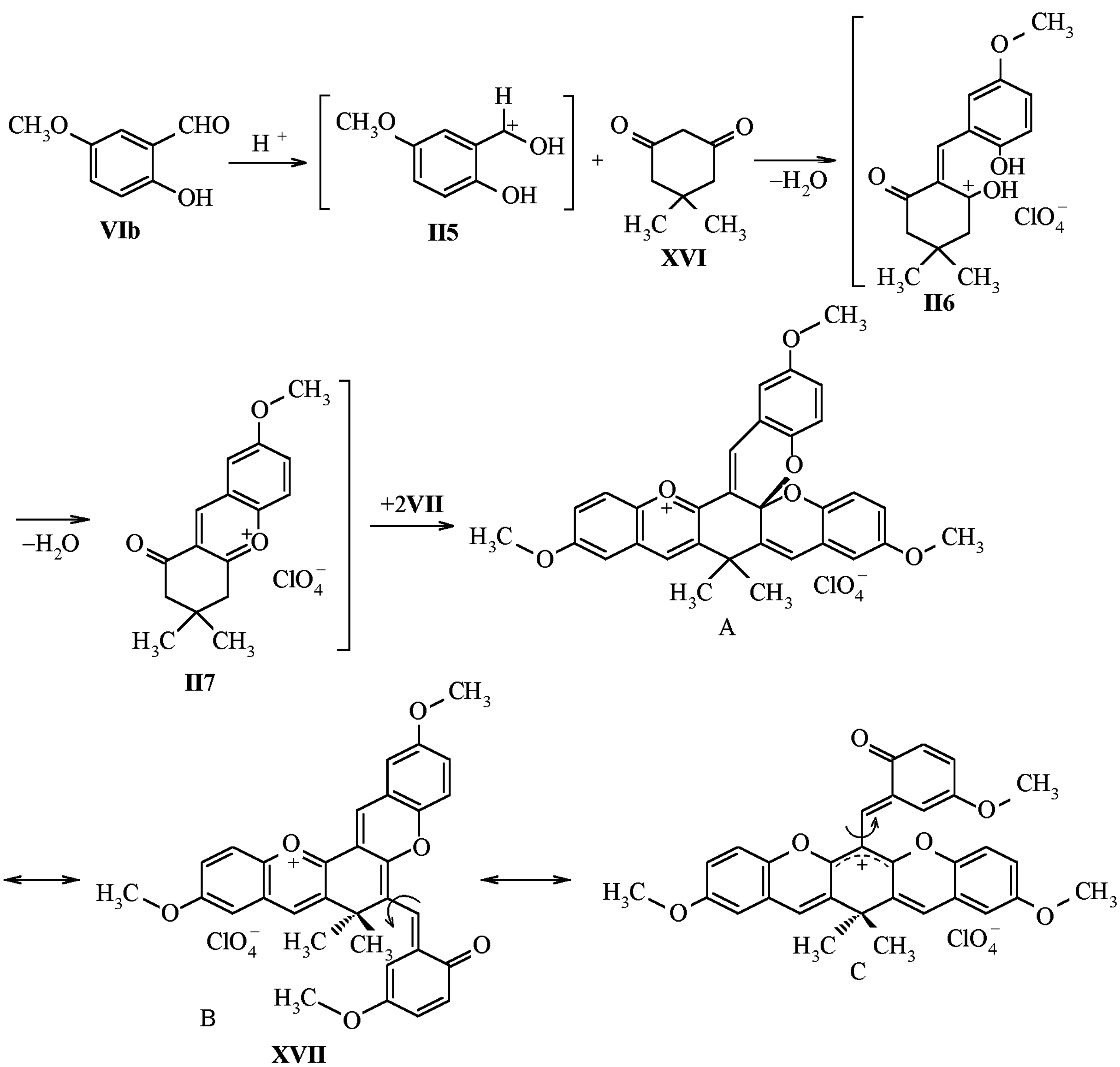
Scheme 4.



form. The ^1H NMR spectra of bromides **XIa–d** are identical to those from the corresponding perchlorates **IX**. The data on IR and ^1H NMR compounds **IX–XII** are presented in Table 5.

In compounds **IX, X, XII** with a common xanthylium core in the electron absorption spectra appear characteristic bands in the longwave region with two maxima at 521 and 558 nm; perchlorate **IXi**

Scheme 5.



$[=H(C_2H_5)_2]$ forms an exception (Table 1). Accordingly in the fluorescence spectra from acetonitrile solutions of compounds **IX, X, XII** are observed two bands of λ^{fl}_{1max} 570 and λ^{fl}_{2max} 620 nm, and for perchlorate **IXi** these bands are present at λ^{fl}_{1max} 537 and λ^{fl}_{2max} 580 nm. The quantum efficiency of fluorescence for these solutions amounts to 0.46–0.95. As seen from Table 1, the substituent R^1 in the dihydroxanthylium ring significantly affects the absorption and fluorescence spectra of perchlorates **VII**, unlike the substituents in the aminoaryl moiety of salts **IX** and **X** whose variation does not result in any changes in the position of the maxima in the absorption and fluorescence spectra. Also there is no significant difference in the spectral characteristics when the aminoaryl fragment of perchlorates **IXa–g** or bases **Xa–d** in position 3 is replaced by an oxygen atom [1,1-dimethyl-1*H*-2,3-dihydroxanthen-3-one (**XII**)].

Since in the Knoevenagel type condensations [9] 1,3-diketones take part when in the carbon triad to the middle carbon (position 2) are attached two hydrogens, it is natural to presume that 2-substituted oxoenols, in particular, 2-bromodimedone, under the applied dehydrating conditions can afford salts **VIII**. Actually, the condensation of 2-bromodimedone (**XIII**) with 2-hydroxyarylaldehydes in triethyl ortho-

Table 5. IR and ^{1}H NMR spectra of derivatives of 1,2-dihydroxanthylium **VIIc, e, g, i; IXb–d, j; Xb; XIIb**

Compd. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm
VIIc	1100, 1246, 1286, 1566, 1633	1.48 s (6H), 1.52 t (3H), 2.78 s (2H), 3.92 s (3H), 4.40 q (2H), 6.41 s (1H), 7.38 d (1H), 7.58 s (1H), 7.70 d (1H), 8.72 s (1H)
VIIe	1090, 1233, 1533, 1606	1.42 t (9H), 2.80 s (2H), 4.38 q (2H), 6.48 s (1H), 7.40 d (1H), 7.45 q (1H), 7.79 d (1H), 8.42 s (1H)
VIIg	1100, 1220, 1513, 1633	1.50 s (6H), 1.52 t (3H), 2.46 s (3H), 2.85 s (2H), 4.45 t (2H), 6.40 s (1H), 7.43 d (1H), 7.55 q (1H), 7.92 d (1H), 8.58 s (1H)
VIIi	1106, 1266, 1553, 1613	1.50 m (9H), 2.90 s (2H), 3.93 s (3H), 4.42 t (2H), 7.42 t (1H), 7.58 s (1H), 7.70 d (1H), 8.58 s (1H)
IXb	1090, 1266, 1540, 1606, 3220	1.52 s (6H), 3.10 s (2H), 3.82 s (3H), 6.10 s (1H), 7.01 d (1H), 7.12 d (1H), 7.15 d (1H), 7.28 m (5H), 7.60 s (1H)
IXc	1100, 1253, 1540, 1606, 3225	1.50 s (6H), 2.40 s (3H), 3.12 s (2H), 3.91 s (3H), 6.15 s (1H), 7.01 d (1H), 7.12 d (1H), 7.19 d (1H), 7.30 q (4H), 7.32 s (1H), 7.59 s (1H)
IXd	1090, 1260, 1540, 1606, 3206	1.50 s (6H), 3.14 s (2H), 3.82 s (3H), 3.96 s (3H), 6.07 s (1H), 6.98 d (1H), 7.12 d (1H), 7.16 d (1H), 7.35 m (5H), 7.64 s (1H)
IXj	1100, 1260, 1553, 1606	1.47 s (6H), 3.08 s (2H), 3.68 m (2H), 3.90 s (3H), 4.25 m (6H), 6.10 s (1H), 6.97 d (1H), 7.09 d (1H), 7.13 d (1H), 7.30 m (4H), 7.60 d (1H)
Xb	1206, 1533, 1573, 1600	1.38 s (6H), 2.33 s (3H), 3.01 s (2H), 4.87 s (3H), 6.02 s (1H), 6.84 d (1H), 6.98 d (1H), 7.07 d (1H), 7.15 m (4H), 7.17 d (1H)
XIIb	1213, 1506, 1580, 1633, 1700	1.39 s (6H), 2.56 s (2H), 3.90 s (3H), 6.32 s (1H), 7.05 d (1H), 7.16 s (1H), 7.30 d (1H), 7.98 s (1H)

Table 6. IR and ^{1}H NMR spectra of 13*H*-chromeno[3,2-*b*]xanth-5-ylium perchlorates **VIII**

Compd. no.	IR spectrum, ν, cm^{-1}	^{1}H NMR spectrum, δ, ppm
VIIIc	1100, 1240, 1500, 1620	1.90 s (6H), 3.98 s (6H), 6.79 s (1H), 7.45 q (4H), 7.33 d (2H), 8.52 s (2H)
VIIIe	1100, 1246, 1273, 1500, 1606	1.77 s (6H), 3.89 s (3H), 6.71 s (1H), 7.79 d (2H), 7.84 m (4H), 8.61 s (2H)
VIIIk	1100, 1286, 1560, 1618	1.76 s (6H), 7.67 m (2H), 7.88 m (6H), 8.35 s (2H)
VIIIl	1090, 1273, 1566, 1593, 1620	1.73 s (6H), 2.51 s (6H), 7.70 m (6H), 8.22 s (2H)
VIIIm	1095, 1270, 1500, 1610, 1633	1.73 s (6H), 2.58 s (6H), 7.50 d (2H), 7.62 s (2H), 7.80 d (2H), 8.28 s (2H)
VIIIn	1090, 1273, 1566, 1585, 1620	1.75 s (6H), 3.96 s (6H), 7.32 d (2H), 7.45 d (2H), 7.75 d (2H), 8.25 s (2H)
VIIIo	1100, 1246, 1540, 1605, 1633	1.73 s (6H), 7.72 m (4H), 7.85 d (2H), 8.24 s (2H)
VIIIp	1090, 1260, 1560, 1585, 1606	1.72 s (6H), 8.05 s (2H), 8.22 s (2H), 8.31 s (2H)
VIIIq	1100, 1260, 1500, 1540, 1606	1.73 s (6H), 7.80 m (4H), 7.91 d (2H), 8.20 s (2H)
VIllr	1095, 1246, 1500, 1553, 1615	1.75 s (6H), 7.90 m (6H), 8.27 s (2H)
VIIIs	1070, 1246, 1546, 1587, 1620	1.75 s (6H), 3.86 d (4H), 5.30 q (4H), 6.18 m (2H), 7.60 t (3H), 7.80 t (3H), 8.31 s (2H)
VIIIt	1100, 1260, 1553, 1566, 1622	1.74 s (6H), 2.53 s (6H), 7.68 s (2H), 7.80 d (2H), 8.30 s (2H)
VIIIu	1090, 1193, 1260, 1500, 1633	1.75 s (6H), 3.28 s (6H), 7.58 d (2H), 7.69 s (1H), 7.82 d (2H), 8.25 s (2H)
VIIIv	1092, 1266, 1540, 1620	1.72 s (6H), 3.90 s (6H), 7.58 d (2H), 8.29 s (2H)

formate in the presence of perchloric acid at the ratio 1 : 2 : 1 afforded perchlorates **VIIIj–u** in 50–70% yield. In acetic anhydride medium containing 16% solution of perchloric acid in acetic acid salts **VIIIj–u** form in lower yield (20–40%). Obviously the yields are reduced by participation of the intermediate acyloxycation P4 in side processes, e.g. transacetylation, under the reaction conditions [13]. With aldehyde of low basicity (e.g., nitrosalicylaldehyde) perchlorate **VIIIo** may form via intermediate diethoxypropenyl cation (**IVb**) (Scheme 3).

When dimedone has an acetyl as a substituent in position 2, then in the condensation take part three molecules of 2-hydroxyarylaldehyde yielding diperchlorate **XV** (Scheme 4).

In its ^{1}H NMR spectrum appear all the signals corresponding by integral intensity and multiplicity to the structure of diperchlorate **XV**.

Under similar conditions unsubstituted dimedone (**XVI**) also affords a product of tris-condensation, 7*H*-chromeno[2,3-a]-xanth-13-ylium (**XVII**) (Scheme 5).

Perchlorate **XVII** may have any of three alternative structures **XVIIA–C**. The ^{1}H NMR data evidence that it exists predominantly as structural isomer **XVIIB**.

Derivatives of xanthylium **VII**, **IX–XII** and 1-benzopyrylium **VIII** are efficient phosphores in the region 530–630 nm. First obtained in this study dihydroxanthylium perchlorates **VII** should be specially mentioned since their quantum efficiency of fluorescence amounting to 0.98 is the highest among the known xanthylium systems [12]. Apparently the main contribution into the absorption and luminescence spectral properties of the molecules originates from the π-system of the dihydroxanthylium ring. These compounds can be also applied as reagents for amino groups detection, also in the fluorescence microscopy [14], and the derivatives of dihydroxanthylium with the substituted ethoxy groups can serve as fluorescent dyes for various applications. The developed synthetic procedures for the known and new perchlorates **VIII** are the easiest and preparative. The conversions revealed extend the theoretical concepts on the reactivity of 1,3-oxoenoles in the acid media and on practical opportunities for preparation of dyes with excellent absorption and luminescent characteristics.

EXPERIMENTAL

IR spectra of the compounds obtained were recorded on spectrometer Specord 71IR from mulls in mineral oil.The ^{1}H NMR spectra were registered on spectrometer Varian VXR-300: perchlorates **VIIIc, e** in deuteroacetone, salts **VIIg, VIIIk–v** in deuteroacetonitrile, compounds **VIIc, e, i, IXb–d, j, Xb, XIIb** in deuterochloroform. Electron absorption spectra were registered on spectrophotometer Specord M-40. The fluorescence spectra and spectra of fluorescence excitation were measured on spectrofluorimeter Elumin 2M. In determination of quantum efficiency of fluorescence rhodamine C was used as standard (φ = 0.73 [15]). Elemental analyses were carried out in the Microanalysis Laboratory of the Research Institute of Physical and Organic Chemistry of Rostov State University.

2-Bromo-5,5-dimethyl-1,3-diethoxycyclohexenylium perchlorate (IVb) was prepared along procedure [6] from 2.2 g (0.01 mol) of 2-bromodimedone (**XIII**), 20 ml of triethyl orthoformate, and 1 ml of 70% perchloric acid. The product was purified by recrystallization from a mixture AcOH–Ac_2O, 10 : 1. Colorless hygroscopic crystals. Yield 3.38 g (91%), mp 81–83°C. IR spectrum, ν, cm^{-1}: 1086, 1286, 1540. ^{1}H NMR spectrum ($CDCl_3$, δ, ppm): 1.03 s (6H), 1.35 t (6H), 2.58 s (4H), 4.42 q (4H). Found, %: C 38.35; H 5.41; Cl 30.68. $C_{12}H_{20}BrClO_6$. Calculated, %: C 38.37; H 5.37; Cl 30.71.

7-Methoxy-3-ethoxy-1,2-dihydroxanthylium perchlorate (VIIa). To a solution of 1.1 g (0.01 mol) of cyclohexane-1,3-dione in 20 ml of triethyl orthoformate was added at stirring 1 ml of 70% perchloric acid. The mixture was left standing at 25°C for 0.5 h, then diluted with anhydrous ether, the upper layer was decanted from the separated oily 1,3-diethoxy1-cyclohexenylium perchlorate (**IVc**), the bottom layer was washed with anhydrous ether (2–20 ml), and 20 ml of triethyl orthoformate and 1.5 g (0.01 mol) of 5-methoxysalicylaldehyde (**VIb**) were added thereto. The mixture was boiled for 30 min with simultaneous distilling off the volatile fractions, then on cooling the separated precipitate was filtered off, washed with ethyl acetate and ether, and purified by recrystallization from acetic acid. Yield 2.94 g (82%), mp 131–132°C. IR spectrum, ν, cm^{-1}: 1086, 1286, 1540, 1606. ^{1}H NMR spectrum [$(CD_3)_2CO$, δ, ppm]: 1.52 t (3H), 3.05 t (2H), 3.39 t (2H), 3.98 s (3H), 4.61 q (2H), 6.65 s (1H), 7.58 t (2H), 7.90 d (1H), 8.67 s (1H). Found, %: C 53.91; H 4.82; Cl 9.87. $C_{16}H_{17}ClO_7$. Calculated, %: C 53.86; H 4.80; Cl 9.94.

1,1-Dimethyl-3-ethoxy-1,2-dihydroxanthylium perchlorates (VIIb–i) (general procedure, Tables 1, 3, 5). (a) To a suspension of 0.01 mol of 2-R-5,5-

dimethyl-1,3-diethoxy-1-cyclohexenylium perchlorate (**IVa, b**) in 20 ml of triethyl orthoformate was added at stirring 0.01 mol of 2-hydroxyarylaldehyde **VI**. The mixture was boiled for 30 min while removing the volatile compounds by distillation. On cooling the separated precipitate was filtered off and recrystallized from acetic acid.

(b) To a solution of 0.01 mol of 2-R-5,5-dimethyl-1,3-diethoxy-1-cyclohexenylium perchlorate (**IVa, b**) in 10 ml of acetic anhydride was added 0.01 mol of 2-hydroxyarylaldehyde **VI**. The mixture was stirred for 15–20 min at 60–70°C and then cooled, diluted with an equal volume of ether, the precipitate was filtered off and recrystallized from acetic acid.

Perchlorates **VIIb–i** prepared along both procedures a and b were identical, no depression of the melting point was observed with the mixed samples.

2,10-Dimethoxy-13*H*-chromeno[3,2-b]xanth-5-ylium perchlorate (VIIIa). 1,3-Diethoxy-1-cyclohexenylium perchlorate (**IVc**) was obtained from 1.1 g (0.01 mol) of cyclohexane-1,3-dione, 20 ml triethyl orthoformate, and 1 ml of 70% perchloric acid. To perchlorate **IVc** was added 40 ml of triethyl orthoformate, 3.0 g (0.02 mol) of 5-methoxysalicylaldehyde, and the mixture was boiled for 30 min while removing volatile compounds by distillation. On cooling 40 ml of acetic acid was added (to dissolve the intermediately arising perchlorate **VIIa**), and the mixture was boiled for 30–40 min. On cooling the separated precipitate was filtered off, washed with ethyl acetate and ether, and purified by recrystallization from nitromethane. Yield 3.0 g (67%), mp 247–249°C. IR spectrum, ν, cm^{-1}: 1100, 1273, 1540, 1606. ^1H NMR spectrum ($CDCl_3$, δ, ppm): 3.91 s (6H), 4.80 s (2H), 6.22 s (1H), 7.10 s (2H), 7.25 d (2H), 7.44 d (2H), 8.08 s (2H). Found, %: C 59.32; H 3.88; C 17.91. $C_{22}H_{17}ClO_8$. Calculated, %: C 59.40; H 3.85; Cl 7.97.

13*H*-Chromeno[3,2-b]xanth-5-ylium perchlorates VIIIb–j (general procedure, Table 2, 4, 6). (a) To a suspension of 0.01 mol of perchlorate **IVa** in 40 ml of triethyl orthoformate was added at stirring 0.02 mol of 2-hydroxyarylaldehyde **VI**. The mixture was boiled for 1 h while distilling off the volatile compounds. On cooling the precipitate was filtered off, washed with ethyl acetate and ether, and purified by recrystallization from nitromethane.

On replacing the triethyl orthoformate with acetic anhydride (20 ml, 60–70°C, 20–30 min) perchlorates **VIIIb–j** were obtained in 20–40% yield.

(b) To a suspension of 0.01 mol of perchlorate **VIIa–f** in 20 ml triethyl orthoformate was added at stirring 0.01 mol of 2-hydroxyarylaldehyde **VI**. The mixture was boiled for 30 min, cooled, the separated crystals were filtered off and treated as in the procedure (a). Perchlorates **VIIIa–i** prepared along both procedures (a) and (b) were identical, no depression of the melting point was observed with the mixed samples.

6-Bromo-13,13-dimethyl-13*H*-chromeno[3,2-b]-xanthylium perchlorates VIIIk–v (general procedure, Tables 2, 4, 6). (a) To a suspension of 0.01 mol of perchlorate **IVb** in 40 ml of triethyl orthoformate was added at stirring 0.02 mol of 2-hydroxyarylaldehyde **VI**. The mixture was boiled for 1 h, cooled, the precipitated crystals were filtered off, washed with ethyl acetate and ether, and purified by recrystallization from nitromethane.

(b) To a suspension of 0.01 mol of perchlorate **VIIh** in 20 ml of triethyl orthoformate was added at stirring 0.01 mol of 2-hydroxyarylaldehyde **VI**. The mixture was boiled for 30 min, cooled, the separated crystals were filtered off and worked up as in the procedure (a).

(c) To a solution of 2.2 g (0.01 mol) of 2-bromodimedone (**XIII**) in 20 ml of triethyl orthoformate was added 0.01 mol of 2-hydroxyarylaldehyde **VI**, and at stirring 1 ml of 70% perchloric acid. The mixture was boiled for 1 h while distilling off the volatile compounds. On cooling in 5–6 h precipitated crystals which were filtered off and worked up as in the procedure (a).

On replacing the triethyl orthoformate with acetic anhydride (10 ml, 60–70°C, 20–30 min) perchlorates **VIIIk–v** were obtained in 20–40% yield.

Perchlorates **VIIb–i** prepared along procedures (a), (b), and (c) were identical, no depression of the melting point was observed with the mixed samples.

3-(R^2,R^3-Amino)-1,2-dihydroxanthylium perchlorates IXa–g (general procedure, Tables 1, 3, 5). To a solution of 0.01 mol of perchlorate **VIIa–h** in 20 ml of acetic acid was added at stirring 0.01 mol of amine. The mixture was boiled for 5 min and cooled, diluted with an equal volume of ether, the precipitate was filtered off, washed with ethyl acetate and ether, and purified by recrystallization from a mixture of nitromethane and 70% perchloric acid, 100 : 1.

3-(R^2,R^3-Amino)-7-methoxy-1,2-dihydroxanthylium perchlorates IXh–j (general procedure, Tables 1, 3, 5). To a solution of 0.01 mol of perchlorate **VIIa–h** in 20 ml of chloroform was added at stirring 0.01 mol of amine. The mixture was boiled for 5 min, cooled, the precipitate was separated and recrystallized from acetic acid.

(2,3-Dihydro-1*H*-xanthen-3-ylidene)-(R^2-phenyl)amines Xa–d (general procedure, Tables 1, 3, 5). To a solution of 0.01 mol of perchlorate **IX** in 20 ml of anhydrous acetone was added at stirring 0.015 mol of anhydrous potassium carbonate. The mixture was stirred for 5–10 min till the solution became light yellow. The precipitate was filtered off, the solution was evaporated, and the residue was purified by recrystallization from methanol.

3-(R^2,R^3-Amino)-1,2-dihydroxanthylium bromides XIa–d (general procedure, Table 3). To a solution of 0.01 mol of imine **X** in 20 ml of ethyl acetate was added dropwise at stirring 0.01 mol of conc. HBr. The precipitate was filtered off, wash ed with ethyl acetate and ether, and purified by reprecipitation with ether from nitromethane solution.

1,1-Dimethyl-1*H*-2,3-dihydroxanthen-3-ones XIIa, b (general procedure, Tables 1, 3, 5). To a solution of 0.01 of perchlorate **VII** in 20 ml of acetone was added 0.012 mol of sodium acetate in 20 ml of water. The mixture was stirred at heating on a water bath till evaporation of acetone. On cooling to room temperature precipitated yellow crystals that were filtered off, washed with water, and purified by recrystallization from aqueous methanol (1:5).

13,13-Dimethyl-2,10-dimethoxy-6-(6-methoxychromylium-2-yl)-13*H*-chromeno[3,2-b]xanth-5-ylium diperchlorate (XV). To a solution of 1.8 g (0.01 mol) of 2-acetyldimedone (**XIV**) in 30 ml triethyl orthoformate was added 4.5 ml (0.03 mol) of 5-methoxysalicylaldehyde (**VIa**), and then at stirring was added 1.5 ml of 70% perchloric acid. After 1.5–2 h the separated crystals were filtered off, washed with ethyl acetate and ether, and recrystallized from nitromethane. Yield 4.9 g (67%), mp 335–337°C. IR spectrum, ν, cm^{-1}: 1090, 1226, 1280, 1560, 1606. ^1H NMR spectrum ($CDCl_3$, δ, ppm): 1.50 s (6H), 3.97 s (3H), 4.03 s (6H), 7.41 d (1H), 7.55 m (3H), 7.80 m (5H), 8.45 s (1H), 8.80 m (3H). Found, %: C 55.71; H 3.80; Cl 9.74. $C_{34}H_{28}Cl_2O_{14}$. Calculated, %: C 55.83; H 3.86; Cl 9.69.

7,7-Dimethyl-2,10-dimethoxy-6-(3-methoxy-6-oxo-2,4-cyclohexadienylidenemethyl)-7H-chromeno-[2,3-a]xanth-13-ylium perchlorate (XVII). To a solution of 1.4 g (0.01 mol) of dimedone (**XVI**) in 30 ml of triethyl orthoformate was added 4.5 ml (0.03 mol) of 5-methoxysalicylaldehyde (**VIa**) and 1.5 ml of 70% perchloric acid. After 12 h the separated crystals were filtered off, washed with ethyl acetate and ether, and recrystallized from acetic acid. Yield 3.7 g (63%), mp 281–284°C. IR spectrum, ν, cm^{-1}: 1100, 1233, 1260, 1540, 1620. ^1H NMR spectrum (CD_3CN, δ, ppm): 1.12 s (3H), 1.85 s (3H), 3.82 s (3H), 3.90 s (3H), 4.02 s (3H), 4.80 s (1H), 6.50 d (1H), 6.70 d (1H), 6.80 d (1H), 7.12 d (1H), 7.15 s (1H), 7.30 s (1N), 7.60 s (1N), 7.93 d (1N), 8.20 d (1N), 8.85 s (1N), 9.31 s (1N). Found, %: S 65.17; N 4.58; Sl 6.05. $S_{32}N_{27}SlO_9$. Calculated, %: S 65.03; N 4.61; Sl 6.00.

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