REACTION OF PERCHLORATES OF CONDENSED THIOPYRYLIUM DERIVATIVES WITH AROMATIC ALDEHYDES

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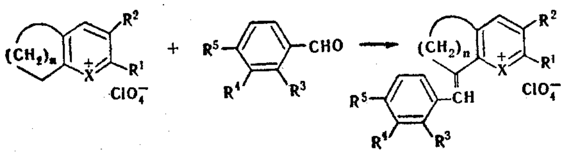
The synthesis of new monomethinecyanines from 2,3-trimethylene- and 2-phenyl-5,6,7,8-tetrahydrothiochromylium, 2-phenyl-5,6-trimethylenethiopyrylium, sym-octahydrothioxanthylium and sym-octahydroxanthylium perchlorates and aromatic aldehydes is described.

Monomethinecyanines are of interest as potential photosensitizers and dyes [1, 2]. In the present communication we describe the synthesis of the new monomethinecyanines (VI-XXII) (Table 1) from sym-octahydrothioxanthylium (I), sym-octahydroxanthylium (II), 2,3-trimethylene-5,6,7,8-tetrahydrothiochromylium (III), 2-phenyl-5,6,7,8-tetrahydrothiochromylium (IV), and 2-phenyl-5,6-trimethylenethiapyrylium (V) perchlorates and aromatic aldehydes:



I-V VI-XXII

VI $X=S$, $n=3$, $R^1—R^2=(CH_2)_4$, $R^3=R^4=H$, $R^5=N(CH_3)_2$; VII $X=S$, $n=3$, $R^1—R^2=(CH_2)_4$, $R^3=OH$, $R^4=R^5=H$; VIII $X=S$, $n=3$, $R^1—R^2=(CH_2)_4$, $R^3=R^4=H$, $R^5=OCH_3$; IX $X=S$, $n=3$, $R^1—R^2=(CH_2)_4$, $R^3=H$, $R^4=R^5=OCH_3$; X $X=O$, $n=3$, $R^1—R^2=(CH_2)_4$, $R^3=R^4=H$, $R^5=N(CH_3)_2$; XI $X=O$, $n=3$, $R^1=R^2=(CH_2)_4$, $R^3=OH$, $R^4=R^5=H$; XII $X=O$, $n=3$, $R^1—R^2=(CH_2)_4$, $R^3=R^4=H$, $R^5=OCH_3$; XIII $X=O$, $n=3$, $R^1—R^2=(CH_2)_4$, $R^3=H$, $R^4=R^5=OCH_3$; XIV $X=O$, $n=3$, $R^1—R^2=(CH_2)_4$, $R^3=R^4=H$, $R^5=NO_2$; XV $X=S$, $n=2$, $R^1—R^2=(CH_2)_4$, $R^3=R^4=H$, $R^5=N(CH_3)_2$; XVI $X=S$, $n=2$, $R^1—R^2=(CH_2)_4$, $R^3=OH$, $R^4=R^5=H$; XVII $X=S$, $n=2$, $R^1—R^2=(CH_2)_4$, $R^3=R^4=H$, $R^5=OCH_3$; XVIII $X=S$, $n=2$, $R^1—R^2=(CH_2)_4$, $R^3=H$, $R^4—R^5=OCH_3$; XIX $X=S$, $n=3$, $R^1=C_6H_5$, $R^2=R^3=R^4=H$, $R^5=N(CH_3)_2$; XX $X=S$, $n=3$, $R^1=C_6H_5$, $R^2=R^3=H$, $R^4=R^5=OCH_3$; XXI $X=S$, $n=2$, $R^1=C_6H_5$, $R^2=R^3=R^4=H$, $R^5=N(CH_3)_2$; XXII $X=S$, $n=2$, $R^1=C_6H_5$, $R^2=R^3=H$, $R^4=R^5=OCH_3$

The reactivity of sym-octahydrothioxanthylium perchlorate (I) is lower than that of the oxygen analog (II). Thus, the condensation of the perchlorate (II) with aromatic aldehydes takes place in 30 min at ~100°C and the yield of the end-products is 60-88%, while in the case of the sulfur analog, (I), the reaction mixture must be boiled (~130°C) for an hour, and the yield of products does not exceed 39% [with the exception of (VI)] (Table 1). 2,3-Trimethylene-5,6,7,8-tetrahydrothiochromylium perchlorate (III), obtained for the first time, is less stable than its analog (I), which explains the lower yields of condensation products (XV-XVIII) (Table 1). Of the aromatic aldehydes, p-dimethylaminobenzaldehyde reacts most readily. In all cases, condensation takes place at the α-methylene group and does not affect the heterocyclic ring, as is shown by the IR spectra of (VI-XXII) (Table 2).

For comparison, Table 2 also gives characteristic frequencies of the thiopyrylium cation in the initial perchlorates. The possible overlapping of the absorption bands of the thiopyrylium cation and of the

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TABLE 1. The Monomethinecyanines (VI-XXII)

Methinecyanine	Mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %
			C	H	Cl	S	C	H	Cl	S	
VI	164—167	$C_{22}H_{26}ClNO_4S$	60,8	5,9	8,5	7,1	60,6	6,0	8,2	7,4	71
VII	213—215	$C_{20}H_{21}ClO_5S$	58,9	5,4	8,8	7,5	58,8	5,1	8,7	7,8	28
VIII	180—181	$C_{21}H_{23}ClO_5S$	59,5	5,7	8,4	7,5	59,6	5,4	8,4	7,6	33
IX	183—185	$C_{22}H_{25}ClO_6S$	58,3	5,4	7,9	6,8	58,3	5,5	7,8	7,1	39
X	181—183	$C_{22}H_{26}ClNO_5$	62,9	6,4	8,8	—	62,9	6,2	8,8	—	71
XI	147—149	$C_{20}H_{21}ClO_6$	60,7	5,2	9,6	—	61,2	5,4	9,0	—	87
XII	164—166	$C_{21}H_{23}ClO_6$	61,9	5,7	8,9	—	61,7	5,6	8,7	—	88
XIII	169—171	$C_{22}H_{25}ClO_7$	60,7	5,7	8,2	—	60,5	5,7	8,1	—	61
XIV	251—253	$C_{20}H_{20}ClNO_7$	57,2	4,7	8,9	—	56,9	4,7	8,4	—	37
XV	280(decomp.)	$C_{21}H_{24}ClNO_4S$	60,1	5,7	8,6	7,5	59,8	5,7	8,4	7,6	48
XVI	210—212	$C_{19}H_{19}ClO_5S$	57,6	5,0	8,8	7,9	57,8	4,8	9,0	8,1	20
XVII	200—201	$C_{20}H_{21}ClO_5S$	59,0	5,0	8,6	7,7	58,8	5,1	8,7	7,8	21
XVIII	202(decomp.)	$C_{21}H_{23}ClO_6S$	57,8	5,4	7,9	7,2	57,5	5,2	8,1	7,3	23
XIX	202—204	$C_{24}H_{24}ClNO_4S$	—	—	8,0	7,5	—	—	7,8	7,0	84
XX	161—162	$C_{24}H_{23}ClO_6S$	—	—	7,8	7,2	—	—	7,5	6,8	44
XXI	206—208	$C_{23}H_{22}ClNO_4S$	—	—	8,2	7,6	—	—	8,0	7,2	91
XXII	189—191	$C_{23}H_{21}ClO_6S$	—	—	7,7	6,9	—	—	7,7	6,9	43

TABLE 2. Absorption Spectra of the Initial Perchlorates (I, IV, and V) and of the Monomethinecyanine Dyes (VI-IX and XV-XXII)

Compound	Characteristic frequencies of the stretching vibrations of the thiapyrylium cation,* ν, cm^{-1}	λ_{max}, nm (log ε)
I	1402 m, 1488 m, 1550 w, 1608 w	275(3,44), 327(3,98)
VI	1390 s, 1503 m, 1588 m, 1600 m	260(4,10), 289(4,08), 391(4,11), 680(4,53)
VII	1392 s, 1500 s, 1551 m, 1596 m	260(3,72), 322(3,71), 490(3,81)
VIII	1390 s, 1513 m, 1555 m, 1597 m	278(4,06), 322(4,11), 515(4,28)
IX	1385—1398 s, 1500—1505 m, 1555 m, 1590 m	258(4,31), 327(4,13), 525(4,30)
XV	1380 s, 1497 m, 1565 m, 1592 m	
XVI	1390 s, 1500 m, 1565 m, 1596 m	
XVII	1390 s, 1500—1507 w, 1560 m, 1590 m	279(4,13), 335(4,16), 545(4,54)
XVIII	1393 s, 1502 m, 1568 m, 1598 m	253(4,20), 326(4,11), 558(4,50)
IV	1410 m, 1493—1497 w, 1569 m, 1597 w	251(4,27), 382(4,29)
XIX	1398 s, 1502 m, 1568—1572 m, 1602 m	271(4,54), 415(4,54), 700(4,99)
XX	1390 s, 1500—1505 m, 1568 m, 1590—1595 w	265 (4,44), 371 (4,26), 560 (4,23)
V	1402 m, 1495 w, 1562 m, 1592 w	248(4,41), 382(4,38)
XXI	1398 s, 1505 m, 1568 m, 1590 m	274(4,39), 420(4,18), 730(4,87)
XXII	1400 s, 1500—1505 m, 1565 m, 1598 m	270(4,59), 375(4,44), 590(4,62)

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*The band at 1590-1680 cm^{-1} overlaps the bands of the stretching vibrations of the aromatic ring.

aromatic ring complicate the interpretation of the spectra of compounds (VI-IX and XV-XXII), but the intense absorption at 1380-1410 cm^{-1}, together with the absorption at 1560-1570 cm^{-1}, can be used to identify the thiapyrylium cation in these compounds [3].

It is known that with an increase in the strain of the ring the frequency of an exocyclic C=C double bond rises [4]. In the spectra of compounds (XXI) and (XXII), unlike those of (XIX) and (XX), absorption appears at 1610 cm^{-1}, which must apparently be ascribed to the stretching vibrations of a double bond at a five-membered ring. Since in the reaction of the perchlorate (III) with aromatic aldehydes the formation of isomers is possible through the methylene groups of the two different alicyclic systems, we compared the spectra of the methinecyanines (XV, XVI, and XVIII) and their analogs (VI, VII, and IX). In agreement with the absorption at 1610 cm^{-1} in the spectra of compounds (XV, XVI, and XVIII) mentioned above, this permits us to consider that condensation takes place through the methylene group of the five-membered ring. In the case of compounds (VI-IX, XIX, and XX) the band at 1610 cm^{-1} is absent.

In the IR spectra of sym-octahydroxanthylium perchlorate (II) and the products of its condensation (X-XIV) absorption bands of the pyrylium cation [5] are observed at 1405-1415, 1480-1500, 1580-1590, and 1605-1615 cm^{-1}. All the compounds investigated are characterized by strong absorption at 620-625 and 1085-1110 cm^{-1} (ClO_4^-).

EXPERIMENTAL

The IR spectra were taken on a UR-20 spectrometer in paraffin oil and hexachlorobutadiene. The electronic spectra were taken on a SF-4A spectrometer in methylene chloride at a concentration of 10^{-3} M.

The perchlorates (I, II, IV, and V) were obtained as described previously [6-8].

2,3-Trimethylene-5,6,7,8-tetrahydrothiochromylium perchlorate (III) was obtained by a known method [6] from 7.8 g (0.04 mole) of 2-[(2-oxocyclopentyl)methyl]cyclohexanone, hydrogen sulfide, and 70% perchloric acid. Yield 6.8 g (58%). Mp 78-81°C (after reprecipitation from chloroform with a 6:1 mixture of ether and benzene). It was identified through its tetrachloroferrate, into which it was converted by the action of a hydrochloric acid solution of ferric chloride [9]; mp 82-84°C from acetic acid. Found %: Cl 36.4; S 8.2. $C_{12}H_{15}ClFeS$. Calculated %: Cl 36.4; S 8.2.

The monomethinecyanines (Table 1) were obtained by condensing equimolar amounts of the perchlorates (I-V) with aromatic aldehydes with heating to 100°C or boiling in glacial acetic acid for 30 min-2 h.

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