REACTION OF α- AND γ-METHYLPYRYLIUM SALTS WITH ORTHOESTERS

G. N. Dorofeenko, V. V. Mezheritskii,
and A. L. Vasserman

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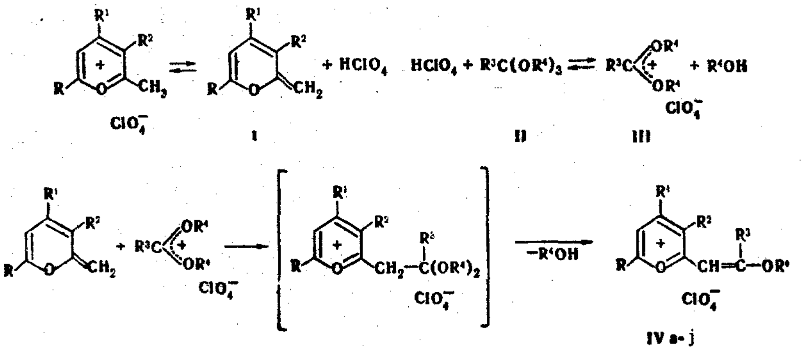
The reaction of orthoesters with α- and γ-methylpyrylium salts gives 2- and 4-alkoxyvinylpyrylium salts the acid hydrolysis of which leads to 2- and 4-hydroxyvinylpyrylium salts and the alkaline hydrolysis to pyranylideneacetaldehydes.

Up to the present time, it has been considered that the reaction of α- and γ-methylpyrylium salts with orthoesters forms only cyanine dyes [1, 2]. The synthesis of these compounds is performed by boiling the reactants in acetic acid in the presence of a basic catalyst. We have shown that when the reaction is performed under milder conditions – by adding the orthoester to a hot (80–85°C) solution of pyrylium salt in glacial acetic acid without subsequent heating – 2- and 4-alkoxyvinylpyrylium salts are formed with yields close to quantitative. It was previously possible to effect such a transformation only in the case of special examples among pyrylium salts condensed with hydrogenated rings where the object of attack by the orthoester was a methylene link [3, 4]. The possibility of the use of α- and γ-methylpyrylium salts considerably broadens the range of applicability of this method, since it permits extremely reactive compounds to be obtained the range of which is practically unlimited, while the methods of preparation are simple.

Monocyclic α- and γ-methylpyrylium salts and related compounds with condensed aromatic nuclei – the 1-benzopyrylium and 2-benzopyrylium salts – take part in the reaction with ethyl orthoformate. Apparently the first stage of this process, as in the synthesis of cyanine dyes, must be the dissociation of the pyrylium salt into the methylene base (I) and a mineral acid. The latter, reacting with the orthoester (II) gives the carboxonium salt (III), the reaction of which with the methylene base and the subsequent splitting off of a molecule of alcohol leads to the ethoxymethylene derivative (IV).



It is probably the inductive, and not the mesomeric, effect of the substituent R^3 that has a decisive influence on the reactivity of the cation (III). This conclusion is in satisfactory harmony with the fact that, because of the +I effect of the alkyl radical R^3, which lowers the positive charge on the carbonium carbon atom of the ion (III), orthoesters of alkylcarboxylic acids (II, $R^3 = CH_3$, C_2H_5) do not react under the conditions

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TABLE 1. Alkoxyvinylpyrylium Perchlorates (IVa-j)

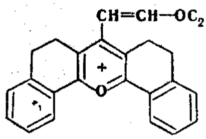
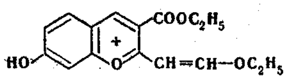
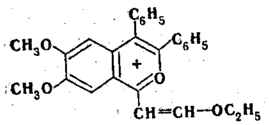
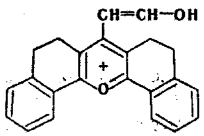
Compound	R	R¹	R²	R³	R⁴	mp, °C	Empirical formula	Found, %			Calculated, %			IR spectra, cm⁻¹	UV spectra		Yield, %
								C	H	Cl	C	H	Cl		λmax, nm	ε · 10⁻³	
IVa	C_6H_5	C_6H_5	H	H	C_2H_5	165	$C_{21}H_{19}ClO_6$	62,7	4,6	8,8	62,5	4,7	8,9	1645, 1590, 1100	725	8,89	95
IVb	$CH_3C_6H_4$	$CH_3C_6H_4$	H	H	C_2H_5	220	$C_{23}H_{23}ClO_6$	64,1	5,3	8,4	64,0	5,3	8,3	1630, 1595, 1100	726	2,65	81
IVc	$C_2H_5OC_6H_4$	$C_2H_5OC_6H_4$	H	H	C_2H_5	215	$C_{25}H_{27}ClO_8$	61,2	5,5	7,5	61,1	5,5	7,3	1635, 1600, 1090	723	3,98	79
IVd	$CH_3OC_6H_4$	$CH_3OC_6H_4$	H	H	C_2H_5	205	$C_{23}H_{23}ClO_8$	59,9	4,8	7,9	59,6	5,0	7,8	1640, 1590, 1095	725	5,94	98
IVe	$(CH_3O)_2C_6H_3$	$(CH_3O)_2C_6H_3$	H	H	C_2H_5	226	$C_{25}H_{27}ClO_{10}$	57,4	5,3	6,2	57,3	5,1	6,8	1640, 1590, 1095	725	1,02	67
IVf	C_6H_5	H	$COOC_2H_5$	H	C_2H_5	162	$C_{18}H_{19}ClO_8$	53,9	4,8	8,9	54,1	4,7	9,0	1640, 1600, 1100	750	5,79	80
IVg	C_6H_5	C_6H_5	H	C_6H_5	CH_3	196	$C_{26}H_{21}ClO_6$	67,3	4,5	7,1	67,1	4,5	7,7	1630, 1610, 1100	510	3,25	75
IVh				H	C_2H_5	245	$C_{25}H_{23}ClO_6$	65,5	4,9	7,8	65,9	5,0	7,9	1635, 1610, 1095	723	5,48	87
IVi				H	C_2H_5	101	$C_{16}H_{17}ClO_9$	46,7	4,3	9,2	46,8	4,4	9,2	3350, 1720, 1640, 1100	723,5	11,92	95
IVj				H	C_2H_5	106	$C_{27}H_{25}ClO_8$	63,1	4,9	7,0	63,2	4,9	6,9	1640, 1590, 1100	650	1,15	92

TABLE 2. Hydorxyvinylpyrylium Perchlorates (Va-g)

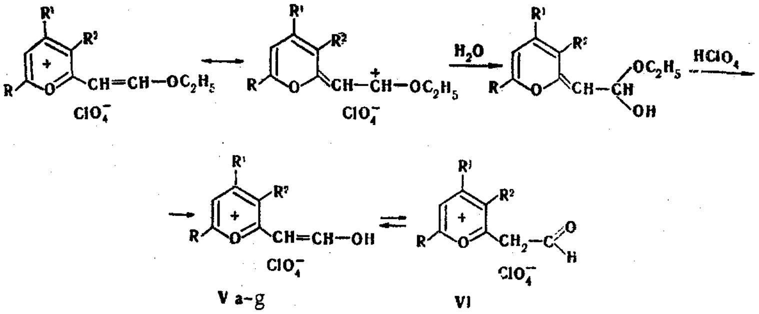
Compound	R	R¹	R²	mp, °C	Empirical formula	Found, %			Calculated, %			IR spectra, cm⁻¹	UV spectra		Yield, %
						C	H	Cl	C	H	Cl		λmax, nm	ε · 10⁻³	
Va	C_6H_5	C_6H_5	H	215	$C_{19}H_{15}ClO_6$	61,2	4,4	9,4	60,8	4,0	9,5	3320, 1630, 1590, 1100	726	3,77	84
Vb	$CH_3C_6H_4$	$CH_3C_6H_4$	H	242	$C_{21}H_{19}ClO_6$	62,6	4,8	8,7	62,5	4,7	8,9	3350, 1640, 1595, 1095	726	1,06	90
Vc	$C_2H_5OC_6H_4$	$C_2H_5OC_6H_4$	H	234	$C_{23}H_{23}ClO_8$	60,4	5,4	7,8	59,6	5,0	7,7	3350, 1640, 1600, 1100	723	1,57	96
Vd	$CH_3OC_6H_4$	$CH_3OC_6H_4$	H	224	$C_{21}H_{19}ClO_8$	57,6	4,3	8,4	57,9	4,3	8,2	3340, 1635, 1590, 1100	724	3,46	82
Ve	$(CH_3O)_2C_6H_3$	$(CH_3O)_2C_6H_3$	H	251	$C_{23}H_{23}ClO_{10}$	55,5	5,0	7,1	55,7	4,9	7,2	3340, 1630, 1590, 1100	723	1,00	84
Vf	C_6H_5	H	$COOC_2H_5$	232	$C_{16}H_{15}ClO_8$	51,5	4,1	9,7	51,7	4,0	9,7	3350, 1720, 1630, 1600, 1095	750	4,04	56
Vg				265	$C_{23}H_{19}ClO_6$	64,5	5,0	8,8	64,6	4,5	8,4	3300, 1640, 1610, 1100	724	5,27	93

considered with pyrylium salts, while methyl orthobenzoate (II, $R^3 = C_6H_5$, $R^4 = CH_3$), in spite of the delocalization of the positive charge on the phenyl substituent, readily react with the same salts.

In the IR spectra of the salts (IVa–j) synthesized there are strong bands in the 1640–1630 cm^{-1} region relating to the stretching vibrations of the pyrylium cation. In all the spectra, the broad band of the C=C double bond of the ethoxyvinyl group overlaps the characteristic band of the pyrylium cation.

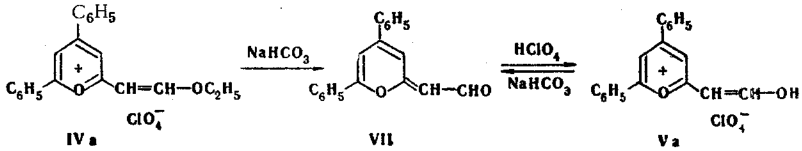
The absorption maxima in the UV spectra of the initial methylpyrylium salts are located in the 250–450 nm region. In the spectra of the salts (IV), new absorption appears in the 500–800 nm region as a consequence of the conjugation of the double C=C bond with the free electron pair of the oxygen of the pyrylium ring. This absorption possesses a low intensity, which makes it possible to assign it to a $n \rightarrow \pi^*$ electronic transition.

Under conditions of acid hydrolysis, the ethoxyvinylpyrylium salts (IV) ($R^3 = H$; $R^4 = C_2H_5$) are converted into the hydroxyvinyl derivatives (Va–g).



The presence in the IR spectra of the salts (Va–g) of a strong band in the 1640–1630 cm^{-1} region, relating to the absorption of the pyrylium cation, and of a band at 3500–3300 cm^{-1}, which is characteristic for an enolic hydroxyl, show that the hydrolysis products exist almost completely in the hydroxymethylene form (V) and not in the carbonyl form (VI). This is also confirmed by the UV spectra [the absorption maxima of the salts (IV) and (V) coincide completely].

The alkaline hydrolysis of the salts (IVa) and (Va) forms the aldehyde (VII).



The action of perchloric acid on (VII) re-forms the hydroxyvinylpyrylium salt (Va). In the IR spectrum of (VII) there is a strong band in the 1680 cm^{-1} region corresponding to the stretching vibrations of a C=O group conjugated with a C=C double bond.

EXPERIMENTAL

The IR spectra were taken on a UR-20 instrument in paraffin oil and the UV spectra on a Specord UV-Vis spectrophotometer in acetic acid. The PMR spectra were recorded on a RYa-2305 spectrometer (60 MHz) in trifluoroacetic acid at room temperature.

6-Ethoxy-2,4-diphenylpyrylium Perchlorate (IVa). To a hot solution of 0.3 g (1 mmole) of 6-methyl-2,4-diphenylpyrylium perchlorate in glacial acetic acid was added 0.4 ml (2 mmoles) of orthoformic ester. On cooling, green crystals of (Va) separated out. PMR spectrum: quadruplet and triplet (3.98 and 1.75 ppm) of an ethyl group, two doublets (5.9 and 5.7 ppm) of vinyl protons, two multiplets (7.64 and 7.3 ppm) of phenyl rings, and a singlet (8.1 ppm) of the protons of a pyrylium ring.

The salts (IVb–j) were obtained similarly (see Table 1).

6-Hydroxymethylene-2,4-diphenylpyrylium Perchlorate (Va). A mixture of 0.4 g (1 mmole) of (IVa) 15 ml of 10% perchloric acid solution, and 2 ml of acetic acid was boiled for 10–15 min, the hot solution was filtered, and on cooling it deposited light yellow crystals of (Va).

The hydroxymethylenepyrylium salts (Vb-g) were obtained similarly (see Table 2).

4,6-Diphenylpyran-2-ylideneacetaldehyde (VII). a) An aqueous solution of sodium bicarbonate was added to 0.4 g (1 mmole) of (IVa) in ether, and the mixture was left for a day. The ethereal extract was dried with anhydrous sodium sulfate, the ether was distilled off, and the substance was recrystallized from petroleum ether. Yield 0.25 g (92.7%), mp 125°C. According to the literature [5], mp 125-126°C.

b) A suspension of 0.17 g (0.5 mmole) of (Va) in ethanol was heated with sodium bicarbonate for 15 min. Then it was filtered, the filtrate was cooled and diluted with water to turbidity, and left for a day. The yield of product was 0.08 g (61.5%), mp 125°C. A mixture with the substance obtained by method (a) gave no depression of the melting point.

LITERATURE CITED

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