REACTIONS OF β-ETHOXYVINYLPYRYLIUM SALTS WITH NUCLEOPHILES

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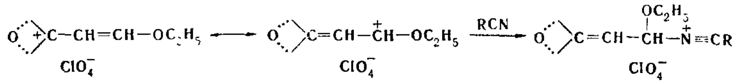
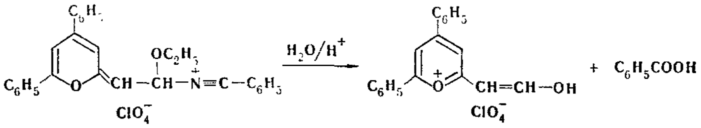
Nitriles, Grignard reagents, and CH-acid compounds attack the β-carbon atom in β-ethoxyvinylpyrylium salts to give, respectively, nitrilium salts, styrylpyrylium salts, and pyrylomerocyanines.

In the present study we have examined the reactions of the previously synthesized [1, 2] β-ethoxyvinylpyrylium salts with some nucleophiles.

2- and 4-Ethoxyvinylpyrylium and benzopyrylium salts add aliphatic and aromatic nitriles at the β-carbon atom to give nitrilium salts:



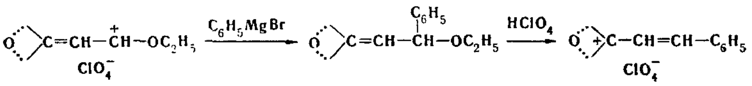
Acid hydrolysis of the nitrilium salts gives β-hydroxyvinylpyrylium salts and carboxylic acids, as shown in the case of perchlorate I:



I II

The isolation of salt II and benzoic acid confirms the proposed structure of perchlorate I. The IR spectrum of I contains a band at 1640-1660 cm^{-1}, which is characteristic for the $C\equiv\overset{+}{N}$ grouping, and bands related to the vibrations of the pyrylium ring, aromatic substituents, and functional groups.

It was shown that 2- and 4-β-ethoxyvinylpyrylium and benzopyrylium salts react with phenylmagnesium bromide and that the attack of the nucleophile is directed to the β-carbon atom of the β-ethoxyvinylpyrylium salt. Treatment of the reaction products with perchloric acid in acetic anhydride gives styrylpyrylium salts.



The structures of the products were confirmed by comparison (mixed-melting-point determinations and IR spectra in the "fingerprint" region) with samples obtained by condensation of methylpyrylium salts with benzaldehyde. Alkyl- and benzylmagnesium bromides apparently also undergo this reaction, but the reaction products cannot be isolated because of their instability.

The possibility of the reaction of 2,4-diphenyl-8-(β-alkoxycycloalkylidene)pyrylium salts with compounds containing an active methylene group was shown in a special example by Kirner and Wizinger [3]. We have extended this reaction to 2- and 4-(β-alkoxyvinyl)pyrylium and benzopyrylium salts. To effect condensation we used malonic, cyanoacetic, and acetoacetic esters, acetylacetone, dibenzoylmethane, and phen-

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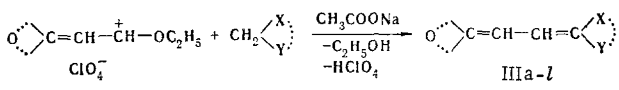
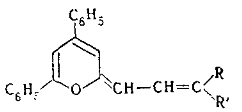
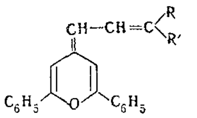
Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 897-900, July, 1974. Original article submitted August 8, 1973.

ylacetic acid. The reaction proceeds with the formation of substances to which we feel it is possible to assign structures III a-*l*:

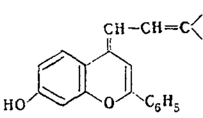




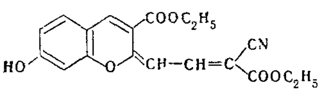
III a-f



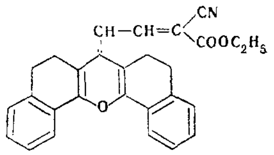
III g, i



III k



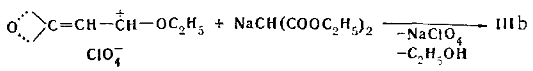
III j



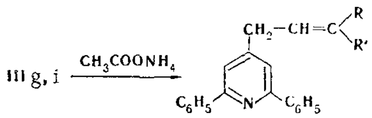
III *l*

IIIa R=CN, R'=$COOC_2H_5$; b R=R'=$COOC_2H_5$; c R=R'=$COCH_3$; d R=R'=COC_6H_5; e R=$COCH_3$, R'=$COOC_2H_5$; f R=C_6H_5, R'=COOH; g R=CN, R'=$COOC_2H_5$; h R==$COCH_3$, R'=$COOC_2H_5$; i R=R'=$COCH_3$

The yields of products III are usually close to quantitative regardless of the structures of the starting pyrylium salt and the methylene-active compounds. To confirm the structures of merocyanines III we accomplished the reaction of 2,4-diphenyl-6-(β-ethoxyvinyl)pyrylium perchlorate with sodiomalonic ester, as a result of which a product identical to IIIb is formed.

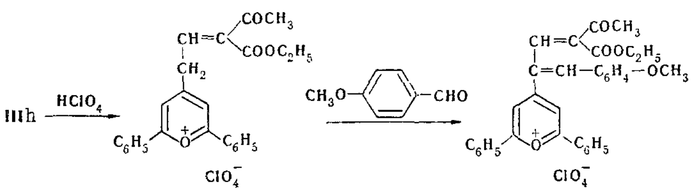


The synthesized pyrylomerocyanines are capable of exchanging a heterocyclic oxygen atom for nitrogen on melting with ammonium acetate to give compounds of the pyridine series:



R,R'=$COCH_3$; R=$COCH_3$; R'=$COOC_2H_5$

Pyrylium salts containing an active methylene group, which undergoes quantitative condensation with anisaldehyde, are obtained by the action of perchloric acid on the pyrylomerocyanines:



The IR spectra of the pyrylomerocyanines contain characteristic absorption bands of the functional groups of pyrylomerocyanines [4, 5].

EXPERIMENTAL

The IR spectra of mineral-oil suspensions of the compounds were obtained with a UR-20 spectrometer.

N-α-Ethoxy-β-[2,4-diphenyl-2-pyranylidene]ethylacetonitrilium Perchlorate (I). A 0.4-g (1 mmole) sample of 2,4-diphenyl-6-(β-ethoxyvinyl)pyrylium perchlorate was refluxed for 20 min with 0.08 ml (1.5 mmole) of acetonitrile in glacial acetic acid. After 24 h, the nitrilium salt was removed by filtration to give 0.42 g (95%) of a product with mp 238° (dec.). IR spectrum: 1640, 1600, and 1100 cm^{-1}. Found: C 62.9; H 4.6; Cl 8.4; N 3.4%. $C_{23}H_{22}NClO_6$. Calculated: C 62.2; H 4.9; Cl 8.0; N 3.2%. Perchlorate II (88%) and benzoic acid (85%) were isolated by acidic hydrolysis of I.

TABLE 1. Synthesized Pyrylomerocyanines

Compound	mp, °C	Empirical formula	Found, %			Calc., %			IR spectrum, cm^{-1}	Yield, %
			C	H	N	C	H	N		
IIIa	152	$C_{24}H_{19}NO_3$	78,3	4,9	4,0	78,1	5,1	3,9	2210, 1720, 1665, 1600	80
IIIb	91	$C_{26}H_{24}O_5$	75,5	5,6	—	75,0	5,8	—	1755, 1710, 1660, 1590	95
IIIc	101	$C_{24}H_{20}O_3$	79,3	5,2	—	80,9	5,6	—	1720, 1680, 1650, 1590	92
IIId	108	$C_{34}H_{24}O_3$	84,9	5,1	—	85,0	5,0	—	1700, 1680, 1650, 1600	40
IIIe	151	$C_{25}H_{22}O_4$	77,7	5,7	—	77,8	5,7	—	1760, 1665, 1640, 1600	98
IIIf	176	$C_{27}H_{20}O_3$	83,2	5,0	—	82,7	5,1	—	1700, 1650, 1600	96
IIIg	162	$C_{24}H_{19}NO_3$	78,3	4,9	4,0	78,2	5,1	3,9	2200, 1700, 1680, 1610	80
IIIh	164	$C_{25}H_{22}O_4$	77,7	5,7	—	77,8	5,7	—	1755, 1660, 1645, 1590	98
IIIi	122	$C_{24}H_{20}O_3$	79,3	5,2	—	79,6	5,8	—	1725, 1680, 1655, 1600	82
IIIj	134	$C_{19}H_{17}NO_6$	64,4	4,4	3,8	64,2	4,8	3,9	3500, 2210, 1725, 1700, 1680, 1610	89
IIIk	142	$C_{22}H_{17}NO_4$	73,1	4,6	3,6	73,5	4,7	3,9	3500, 2210, 1760, 1700, 1640, 1600	90
III*l*	153	$C_{28}H_{23}NO_3$	79,7	5,4	3,3	79,8	5,5	3,3	2210, 1700, 1665, 1595	87

The following compounds were similarly obtained. N-α-Ethoxy-β-[2,4-diphenyl-2-pyranylidene]ethyylbenzonitrilium perchlorate with mp 289° (dec.) was obtained in 88% yield. IR spectrum: 1645, 1600, and 1095 cm^{-1}. Found: C 65.5; H 4.6; Cl 7.2; N 2.6%. $C_{28}H_{24}NClO_6$. Calculated: C 66.4; H 4.7; Cl 7.0; N 2.7%; N-α-Ethoxy-β-[2,6-diphenyl-4-pyranylidene]ethylbenzonitrilium perchlorate with mp 300° (dec.) was obtained in 85% yield. IR spectrum: 1645, 1600, and 1100 cm^{-1}. Found: C 66.7; H 4.6; Cl 8.0; N 2.6%. $C_{28}H_{24}NClO_6$. Calculated: C 66.4; H 4.7; Cl 7.0; N 2.7%; N-α-Ethoxy-β-[7-hydroxy-4-flavenyl]-ethylbenzonitrilium perchlorate with mp 216° was obtained in 82% yield. IR spectrum: 1660, 1610, and 1100 cm^{-1}. Found: C 63.0; H 4.5; Cl 7.0; N 2.4%. $C_{26}H_{22}NClO_7$. Calculated: C 62.9; H 4.4; Cl 7.2; N 2.8%.

2,4-Diphenyl-6-styrylpyrylium Perchlorate. A Grignard reagent obtained from 0.83 ml of bromobenzene and 0.2 g of magnesium in 10 ml of absolute ether was added rapidly to a suspension of 0.8 g (2 mmole) of 2,4-diphenyl-6-β-ethoxyvinylpyrylium perchlorate in 30 ml of dry ether, and the resulting solution was stirred for 20-30 min. The mixture was then decomposed with cold ammonium chloride solution, and the ether layer was separated, washed with 1 N sodium carbonate solution and water, and dried with calcium chloride. Acetic anhydride (2 ml) and 0.2 ml (2 mmole) of 70% perchloric acid were added to the ether solution, and the mixture was worked up to give 0.65 g (75%) of a product with mp 233° [6]. The following compounds were similarly obtained. 2,6-Diphenyl-4-styrylpyrylium perchlorate with mp 252-253° [6] was obtained in 69% yield. 4-Styrylflavylium perchlorate with mp 240° was obtained in 71% yield. Found: C 67.4; H 4.6; Cl 8.6. $C_{23}H_{17}ClO_5$. Calculated: C 67.4; H 4.1; Cl 8.7%.

Ethyl α-Carbethoxy-γ-pyranylidene-4-crotonate. A 0.4-g (1 mmole) sample of 2,4-diphenyl-6-β-ethoxyvinylpyrylium perchlorate and 0.16 ml (1 mmole) of malonic ester were refluxed in acetic anhydride for 10 min. Sodium acetate [0.08 g (1 mmole)] was added, and the mixture was refluxed for another 30 min. It was then cooled and diluted with 10 ml of water. After 24 h, the mixture was filtered to give 0.4 g of IIIb. A similar procedure was used to obtain IIIa-*l* (see Table 1).

A 0.18-g (1 mmole) sample of sodiomalonic ester was added to a suspension of 0.4 g (1 mmole) of 2,4-diphenyl-6-β-ethoxyvinylpyrylium perchlorate in dry ether. After a few hours, the sodium perchlorate was removed by filtration, ether was removed by distallation, and the residue was refluxed for 10-15 min in acetic anhydride. The mixture was diluted with water and extracted with ether, and the extract was dried with sodium sulfate. The ether was removed by distillation to give IIIb.

1-Acetyl-1-carbethoxy-3-[2,6-diphenyl-4-pyridyl]-1-propene. A 0.4-g (1 mmole) sample of IIIh was fused with ammonium acetate, and the mixture was poured into the minimum amount of water. The mixture was worked up to give 0.38 g (100%) of a product with mp 129-130° (from isopropyl alcohol). IR spectrum: 1750, 1665, 1640, and 1600 cm^{-1}. Found: C 78.3; H 5.7; N 3.7%. $C_{25}H_{23}NO_3$. Calculated: C 78.1; H 5.8; N 3.6%. A similar procedure was used to obtain 1,1-diacetyl-3-[2,6-diphenyl-4-pyridyl]-1-propene with mp 144° in 86% yield. IR spectrum: 1720, 1665, 1650, and 1600 cm^{-1}. Found: C 81.7; H 5.8; N 3.2%. $C_{24}H_{21}NO_2$. Calculated: C 81.1; H 5.9; N 3.9%.

1-Acetyl-1-carbethoxy-3-[2,6-diphenyl-4-pyrylium]-1-propene. A 0.1-ml (1 mmole) sample of 70% perchloric acid was added to 0.4-g (1 mmole) of IIIh in acetic anhydride, and the mixture was diluted with dry ether. The resulting precipitate was removed by filtration to give 0.46 g (97%) of a product with mp 289° (from acetic acid). IR spectrum: 1750, 1665, 1640, 1620, 1600, and 1100 cm^{-1}. Found: C 61.6; H 5.2; Cl 7.8%. $C_{25}H_{23}ClO_8$. Calculated: C 61.6; H 4.7; Cl 7.3%.

1-Acetyl-1-carbethoxy-3-[2,6-diphenyl-4-pyrylium]-4-(p-methoxyphenyl)1,4-butene. A 0.1-ml (1 mmole) sample of 70% perchloric acid and 0.12 ml (1 mmole) of anisaldehyde were added to a solution of 0.4 g (1 mmole) of IIIh in acetic anhydride, and the mixture was refluxed for ~ 1 h. It was then worked up to give 0.6 g (100%) of a product with mp 300° (dec.). IR spectrum: 1720, 1640, 1620, 1590, and 1100 cm^{-1}. Found: C 65.7; H 4.8; Cl 5.1%. $C_{33}H_{29}ClO_9$. Calculated: C 65.4; H 4.8; Cl 5.8%.

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