VINYLPYRYLATION OF AROMATIC COMPOUNDS

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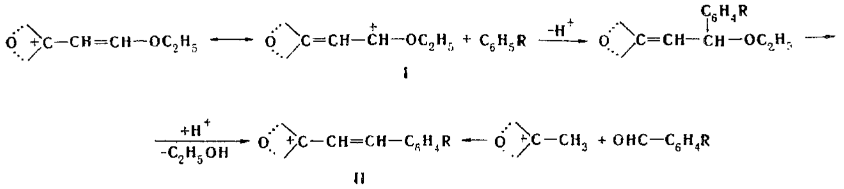
UDC 547.813

The reaction of β-ethoxyvinylpyrylium salts with aromatic compounds gives styrylpyrylium salts, which are also formed from methylpyrylium salts, ethyl orthoformate, and aromatic compounds. The previously unknown phenomenon of attack by a carbonium cation on the meta position of a benzene ring passivated by a nitro group (nitrobenzene) was detected.

It is known [1, 2] that the β-carbon atom in β-ethoxyvinylpyrylium salts is the active center in reactions with nucleophiles. It might have been expected that its high electrophilicity would prove to be sufficient for reaction with aromatic compounds.

It was found that β-ethoxyvinylpyrylium and benzopyrylium salts react with aromatic benzoid and heterocyclic compounds on refluxing in acetic anhydride to give styrylpyrylium salts II via the scheme



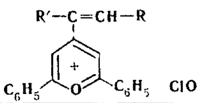
The relative reactivities of β-ethoxyvinylpyrylium salts were studied in the case of an active nucleophile – N,N-dimethylaniline. 4-β-Ethoxyvinylbenzopyrylium salt and monocyclic 4-β-ethoxyvinyl- and 4-β-phenyl-α-ethoxyvinylpyrylium salts undergo this reaction. In the case of monocyclic 2-β-ethoxyvinylpyrylium salts, 2-styrylpyrylium salts could not be isolated under the same conditions. Benzene itself and substituted benzenes containing both electron-donor and electron-acceptor substitutents can participate in this transformation; this was shown in the case of the reaction of 2,6-diphenyl-4(β-ethoxyvinyl)pyrylium perchlorate. In the case of monosubstituted benzenes with electron-donor groups (NR_2, OH, OR, and Cl), para substitution occurs to give products in yields close to quantitative; this was established by alternative synthesis of the samples by condensation of methylpyrylium salts with the appropriate aldehydes. The para carbon atom with respect to one of the methoxy groups is attacked in veratrole, while 2,4-dihydroxystyrylpyrylium salts, which are used for the synthesis of spiropyrans [3], are formed in the case of resorcinol.

An interesting fact that indicates the exceptionally high electrophilicity of the β-carbon atom in β-ethoxyvinylpyrylium salts is the reaction of these compounds with nitrobenzene. In this case the meta position of the nitrobenzene molecule is attacked to give 4-(m-nitrostyryl)-2,6-diphenylpyrylium perchlorate, which is identical to a sample obtained by condensation of 2,6-diphenyl-4-methylpyrylium perchlorate with m-nitro-benzaldehyde. This is apparently the first noted instance of alkylation of a nitro-group-passivated benzene ring by a carbonium ion. The diverse alkylation, formylation, and acylation reactions of aromatic compounds, the essence of which consists in attack on the aromatic ring by a carbonium cation, are not realized in benzoid systems with strong electron-acceptor substituents such as the nitro group.

The reaction of salts I with indole occurs in the β-position of the pyrrole ring and gives a quantitative yield of β-(3-indolyl)vinyl derivative, which is identical to a sample obtained by condensation of 2,6-diphenyl-4-methylpyrylium perchlorate with β-formylindole.

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 6, pp. 743-745, June, 1974. Original article submitted July 24, 1973.

TABLE 1. Styrylpyrylium Salts



Compound	R	R′	Reaction time, h	mp, °C	Empirical formula	Found, %				Calc., %				Yield, %	
						C	H	Cl	N	C	H	Cl	N	A	B
IIa	$C_6H_4NO_2$(p) m-NO_2—C_6H_4	H	8	281	$C_{28}H_{18}ClNO_7$	62,8	4,0	7,4	3.0	62,5	3,7	7,4	2,9	37,5	30
IIb	C_6H_5	H	5	255[4]	$C_{25}H_{19}ClO_5$	—	—	—	—	—	—	—	—	52	50
IIc	C_6H_4OH(p) m-HO—C_6H_5	H	5	264[4]	$C_{25}H_{19}ClO_6$	—	—	—	—	—	—	—	—	58	55
IId	2,5-$(OH)_2C_6H_3$	H	5	272	$C_{25}H_{19}ClO_7$	64,0	4,2	7,4	—	64,2	4,1	7,6	—	62	57
IIe	p-Cl-C_6H_4	H	3	300(decomp.)	$C_{25}H_{18}Cl_2O_5$	64,3	4,0	15,4	—	64,4	3,8	15,1	—	66	60
IIf	p-$N(C_2H_5)_2$—C_6H_4	H	1	285	$C_{29}H_{28}ClNO_5$	68,5	5,1	7,1	3,1	68,8	5,5	7,0	2,8	80	—
IIg	p-C_2H_5O-C_6H_5	H	1	248	$C_{27}H_{23}ClO_6$	67,5	5,5	7,1	—	67,6	4,8	7,4	—	80	—
IIh	3,4-$CH_3O_2C_6H_3$	H	1	253	$C_{27}H_{23}ClO_7$	65,1	4,8	7,4	—	65,1	4,7	7,2	—	89	—
IIi	p-$N(CH_3)_2$-C_6H_4	H	2	288	$C_{27}H_{24}ClNO_5$	67,6	5,0	7,4	3,0	67,8	5,0	7,4	3,0	100	97
IIj	p-$CH_3OC_6H_4$	H	1	270[4]	$C_{26}H_{21}ClO_6$	—	—	—	—	—	—	—	—	100	—
IIk	β-Indolenyl	H	1	300(decomp.)	$C_{27}H_{20}ClNO_5$	68,4	4,1	7,4	3,0	68,4	4,2	7,5	2,9	100	100
IIl	p-$N(CH_3)_2C_6H_4$	C_6H_5	1	300(decomp.)	$C_{33}H_{28}ClNO_5$	71.4	5,4	6,7	2,6	71,4	5,1	6,4	2,5	100	—

The preparation of the styrylpyrylium salts can be realized in a single step by refluxing the methylpyrylium salts with ethyl orthoformate and the aromatic compound in acetic anhydride without isolation of the intermediate β-ethoxyvinyl derivatives. The reaction probably proceeds through the intermediate formation of I. Another possible path – through the intermediate formation of acetals of aromatic aldehydes – should be excluded, inasmuch as we did not observe their formation on refluxing the aromatic compounds with ethyl orthoformate under the reaction conditions. Three-component condensations of heterocyclic systems containing an active methyl group with ortho esters and aromatic compounds were unknown until the present research.

The IR spectra of the compounds obtained have an intense band at 1630-1650 cm^{-1}, which is related to vibrations of C=C bonds conjugated with the pyrylium cation and bands characteristic for the vibrations of the pyrylium ring, benzene rings, and functional substituents.

EXPERIMENTAL

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

4-β-(N,N-dimethylamino)styryl-7-hydroxyflavylium Perchlorate. A) A 0.4-g (1 mmole) sample of 4-β-ethoxyvinyl-7-hydroxyflavylium perchlorate and 0.42 ml (3 mmole) of N,N-dimethylaniline were refluxed in acetic anhydride for 1 h. The mixture was cooled and filtered to give 0.46 g (100%) of the styrylpyrylium salt with mp 300° (decomp.). IR spectrum: 3500, 1645, 1600, and 1100 cm^{-1}. Found: C 64.0; H 4.5; Cl 7.6; N 2.8%. $C_{25}H_{22}ClNO_6$. Calculated: C 64.1; H 4.7; Cl 7.6; N 2.8%. A similar procedure was used to obtain IIa-*l*, the physical constants and yields of which are presented in Table 1; 4-β-(N,N-dimethylamino)strylflavylium perchlorate, with 300° (decomp.), was obtained in 100% yield. IR spectrum: 1650, 1600, and 1100 cm^{-1}. Found: C 66.5; H 4.5; Cl 8.0; N 3.1%. $C_{25}H_{22}ClNO_5$. Calculated: C 66.4; H 4.9; Cl 7.9; N 3.1%; 2,8,9-dibenzo-5-[β-(N,N-dimethylamino)] styryl-3,4,6,7-tetrahydroxanthylium perchlorate, with mp 268°, was obtained in 94% yield. IR spectrum: 1645, 1590, and 1100 cm^{-1}. Found: C 70.5; H 5.4; Cl 6.5; N 2.6%. $C_{31}H_{28}ClNO_5$. Calculated: C 70.2; H 5.3; Cl 6.7; N 2.6%.

B) A 0.3-g (1 mmole) sample of 4-methyl-7-hydroxyflavylium perchlorate, 0.16 ml (1 mmole) of ethyl orthoformate, and 0.14 ml (1 mmole) of N,N-dimethylaniline were refluxed for 1.5 h in acetic anhydride. The mixture was then cooled, and the resulting shiny-green plates were removed by filtration to give 0.45 g (98%) of a product with mp 300° (decomp.). A similar procedure was used to obtain styrylpyrylium salts IIa-e,i,k.

Condensation of Methylpyrylium Salts with Aromatic Aldehydes. A 1-mole sample of the methylpyrylium salt and 1.5 mole of aldehyde were refluxed in acetic anhydride for 0.5-1.5 h. The styrylpyrylium salts crystallized on cooling.

LITERATURE CITED

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