ETHYNYL CARBONIUM IONS.

2.* REACTIONS OF 4-ETHYNYLPYRYLIUM PERCHLORATES WITH ALCOHOLS AND NITROGEN-CONTAINING NUCLEOPHILES

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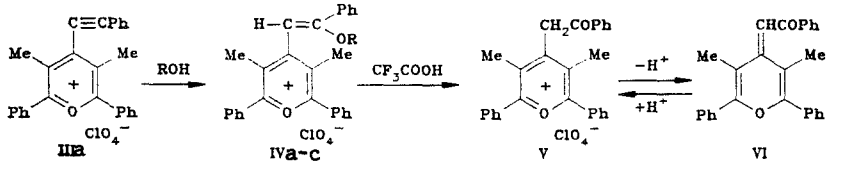
Derivatives of β-alkoxy- and β-(phenylamino)styrylpyrylium salts, the hydrolysis of which leads to phenacylpyrylium salts and 4-benzoylmethylenepyrans, are formed in the reaction of 4-phenylethynylpyrylium salts with alcohols and aromatic amines. Ethynyl-substituted pyridines and pyridinium salts were synthesized by the action of ammonium acetate and methylamine, benzylamine, and butylamine. A β-methylaminostyryl-1-methyl-substituted pyridinium salt is formed with excess methylamine.

Under the influence of oxygen-containing nucleophiles ROH, 2,6-diaryl-4-phenylethynylpyrylium perchlorates that are not substituted in the 3 and 5 positions of the pyrylium ring form monomethinecyanines,† the compositions of which do not include an R residue [1].

In the present research we investigated the reactions of tri- and tetrasubstituted phenylethynylpyrylium salts with alcohols and amines, in the course of which products of ionic addition of the nucleophile to both the triple bond and to the α-carbon atom of the pyrylium ring could be formed.

We found that the principal product (as for β-unsubstituted 4-phenylethynylpyrylium salts) when 2,6-diphenyl-3-methyl-4-phenylethynylpyrylium perchlorate (I) is refluxed with ethanol is a monomethinecyanine – 2,6-diphenyl-3-methyl-4-[1'-(2",6"-diphenyl-3"-methyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyrylium perchlorate (II).

The introduction into the 3 and 5 positions of the 4-ethynylpyrylium cation of methyl groups, which decrease the positive charge in the ring and thereby decrease the electron-acceptor effect of the pyrylium cation on the triple bond, made it possible to isolate products of addition of ROH to the triple bond, viz., IV. Under the influence of CF_3COOH alkoxystyrylpyrylium salts IVa-c are converted extremely easily to phenacylpyrylium salt V and 4-benzoylmethylenepyran VI.



IV [a] R=CH_3; b R=C_2H_5; c R=*i*-C_3H_7

On refluxing in acetonitrile with 2,6-diphenyl-4-phenylethynylpyrylium perchlorate benzoylmethylenepyran VI forms cyanine VII, which is converted to a pyridine; this confirms our assumption regarding the pathway of the formation of monomethinecyanines [1].

The PMR spectrum of pyridine VIII [2.27 ppm (6H, s, $2CH_3$), 6.0 (2H, s, protons in the 3 and 5 positions of pyran ring B), 6.32 (1H, s, =CH), 7.05-7.75 ppm (30H, m, Ar)] provides evidence in favor of the proposed structure VIII, since if the B ring were a pyridine ring,

*See [1] for Communication 1.

†The monomethinecyanine obtained from triphenylethynylcarbinol and a number of its derivatives were first described in [2].

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TABLE 1. Characteristics of IX-XXII and XXIV-XXVII

Compound	Ar	R	R¹	R²	Empirical formula	mp, °C	Reaction conditions		Yield, %
							T, °C	time, h	
IX	Ph	H	H	Ph	$C_{31}H_{24}ClNO_5$	251	−5...0	2	84
X	$C_6H_4OCH_3$-*p*	H	H	Ph	$C_{33}H_{28}ClNO_7$	239	82	2	67
XI	$C_6H_4OCH_3$-*p*	H	H	$C_6H_4CH_3$-*p*	$C_{34}H_{30}ClNO_7$	257...258	−5...20	3	55
XII	Ph	CH_3	H	Ph	$C_{33}H_{28}ClNO_5$	235...236	20	0,5	89
XIII	Ph	CH_3	H	$C_6H_4CH_3$-*p*	$C_{34}H_{30}ClNO_5$	227...228	−5...0	0,5	72
XIV	Ph	CH_3	CH_3	Ph	$C_{34}H_{30}ClNO_5$	180	−5...0	0,5	94
XV	Ph	CH_3	H	$C(CH_3)_3$	$C_{31}H_{32}ClNO_5$	216...217	−5...0	0,5	81
XVI	Ph	H	—	Ph	$C_{31}H_{23}NO$	163...164	20	0,25	81
XVII	$C_6H_4OCH_3$-*p*	H	—	Ph	$C_{33}H_{27}NO_3$	165...166	20	0,25	89
XVIII*	$C_6H_4OCH_3$-*p*	H	—	$C_6H_4CH_3$-*p*	$C_{34}H_{29}NO_3$	172...173	20	0,5	88
XIX	Ph	CH_3	—	Ph	$C_{33}H_{27}NO$	161...162	20	0,25	95
XX	Ph	H	—	—	$C_{25}H_{19}NO$	137**	—	—	69
XXI	$C_6H_4OCH_3$-*p*	H	—	—	$C_{27}H_{23}NO_3$	130...131	—	—	85
XXII	Ph	CH_3	—	—	$C_{27}H_{23}NO$	195...196	—	—	81
XXIV	Ph	H	—	—	$C_{25}H_{17}N$	141...142	—	—	15
XXV	$C_6H_4OCH_3$-*p*	H	—	—	$C_{27}H_{21}NO_2$	123...124	—	—	18
XXVI	Ph	CH_3	—	—	$C_{27}H_{21}N$	142	—	—	72
XXVII	$C_6H_4OCH_3$-*p*	CH_3	—	—	$C_{29}H_{25}NO_2$	161...162	—	—	71

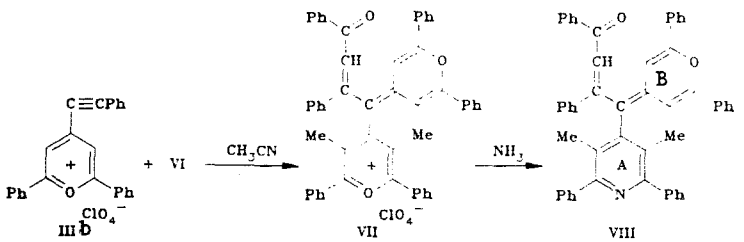
*For XVIII the molecular mass found was in agreement with the calculated value.
**The melting point coincides with the melting point presented in [11].

TABLE 2. Spectral Characteristics of the Synthesized Compounds

Compound	IR spectrum, ν, cm^{-1}	PMR spectrum,* δ, ppm
IX	3234, 1640, 1600, 1580, 1214, 1100	6,37 (1H, s, =CH); 7,35...7,97 (22H, m, Ar)
X	3200, 1640, 1607, 1540, 1260, 1100	3,87 (6H, $2OCH_3$); 6,3 (1H, s, =CH); 6,82...8,0 (20H, m, Ar)
XI	3267, 1634, 1607, 1254, 1100	2,3 (3H, s, CH_3); 3,8 (6H, s, $2OCH_3$); 6,2 (1H, s, =CH); 6,52...8,07 (20H, m, 19H Ar, 1H NH)
XII	3276, 1619, 1600, 1594, 1580, 1554, 1520, 1234, 1100	2,12 (6H, s, $2CH_3$); 5,75 (1H, s =CH); 6,92...7,7 (20H, m, Ar); 9,15 (1H, s, NH)
XIII	3234, 1620, 1600, 1294, 1100	1,93 (6H, s, $2CH_3$); 2,27 (3H, s, CH_3); 6,11 (1H, s, =CH); 7,0...7,8 (20H, m, 19H Ar, 1H NH)
XIV	1610, 1600, 1570, 1100	2,19 (6H, s, $2CH_3$); 3,7 (3H, s, CH_3); 5,95 (1H, s, =CH); 7,02...7,65 (20H, m, Ar)
XV	3260, 1620, 1580, 1600, 1500, 1273, 1100	1,6 (9H, s, $C(CH_3)_3$); 1,81 (6H, s, $2CH_3$); 5,9 (1H, s, =CH); 7,27...7,75 (16H, m, 15H Ar, 1H NH)
XVI	1660, 1580, 1554, 1285	5,47 and 5,85(2H, s, 3 and 5H of pyran ring); 6,25 (1H, s, =CH), 6,82...7,82 (20H, m, Ar)
XVII	1660, 1607, 1554, 1254	3,67 (6H, s, $2OCH_3$); 5,37 and 5,67(2H, s, 3 and 5H of pyran ring); 6,16 (1H, s, =CH); 6,52...7,82 (18H, m, Ar)
XVIII	1660, 1613, 1580, 1554, 1254	2,25 (3H, s, CH_3); 3,65 (6H, s, $2OCH_3$); 5,4 and 5,67 (2H, s, 3 and 5H of pyran ring); 6,1 (1H, s, =CH); 6,5...7,8 (17H, m, Ar)
XIX	1640, 1580, 1545, 1240	1,67 (6H, d, $2CH_3$); 5,45 (1H, s, =CH); 6,82...8,25 (20H, m, Ar)
XX	1678, 1600, 1580, 1554, 1207	4,1 (2H, s, CH_2); 6,95...8,15 (17H, m, Ar)
XXI	1675, 1600, 1574, 1547, 1247	3,7 (6H, s, $2OCH_3$); 4,2 (2H, s, CH_2); 6,7...8,2 (15H, m, Ar)
XXII	1680, 1594, 1580, 1554, 1200	2,1 (6H, s $2CH_3$); 4,37 (2H, s, CH_2); 7,02...8,1 (15H, m, Ar)
XXIV	2220, 1607, 1550	—
XXV	2220, 1614, 1540, 1520, 1254	
XXVI	2210, 1600, 1540	2,45 (6H, s $2CH_3$); 7,0...7,65 (15H, m, Ar)
XXVII	2225, 1605, 1575, 1510, 1245	2,47 (6H, s, $2CH_3$); 3,75 (6H, s, $2OCH_3$); 6,72, 7,62 (13H, m, Ar)

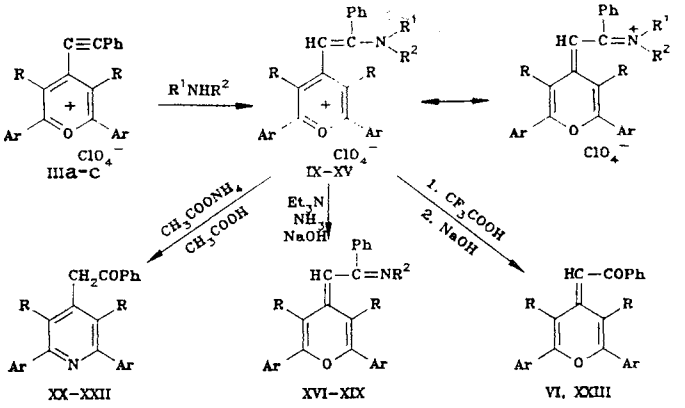
*The PMR spectra of IX-XI were recorded in d_7-DMF, while the PMR spectra of XII-XXII and XXIV-XXVII were recorded in $CDCl_3$.

signals of pyran protons at 6.0 ppm would be absent, and the protons of the methyl groups of the A ring would appear at 1.8-2.0 ppm, as in the case of pyran VI.



According to the investigations the addition of alcohols to ethynyl-substituted pyrylium salts excludes the use of a catalyst, while the search for catalysts for the hydration of alkynes to carbonyl compounds that would surpass the most effective catalyst, mercury acetate, still remains an urgent task [3, 4].

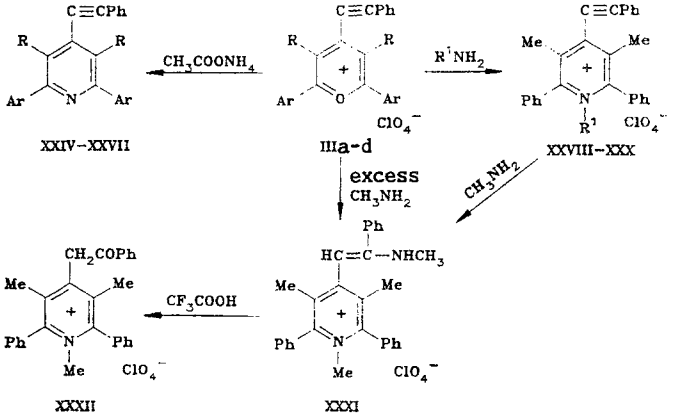
Continuing the study of ethynyl-substituted pyrylium salts we subjected them to reaction with aromatic amines, ammonium acetate, and methyl-, butyl-, and benzylamine. Like alcohols, aromatic amines - aniline, p-toluidine, and N-methylaniline - as well as tert-butylamine, add to the β-carbon atom of the triple bond to give aryl(tert-butyl)aminostyrylpyrylium salts IX-XV, in contrast to 2,4,6-triarylpyrylium salts, which react with aromatic amines to give N-substitute pyridinium salts [5]



III c R=H, Ar=$C_6H_4OCH_3$-*p*

Exchange of oxygen for nitrogen, which is typical for pyrylium salts, does not occur on treatment of IX-XII with ammonia; instead, one observes deprotonation (triethylamine and dilute alkalis act similarly), which is explained by localization of the positive charge on the nitrogen atom in the side chain. 1-(2′,6′-Diaryl-4′-pyranylidene)-2-phenyliminoethanes XVI-XIX, the protonation of which leads to starting derivatives IX-XII, were obtained in good yields. When R^2 = tert-butyl group (XV), deprotonation becomes impossible. The hydrolysis of IX and XII leads to the formation of benzoylmethylenepyrans VI and XXIII. Styrylaminophenylpyrylium salts IX, X, and XII are converted to the corresponding phenacylpyridines XX-XXII by the action of ammonium acetate in acetic acid, i.e., hydrolysis to phenacylpyrylium salts with replacement of the ring oxygen atom by a nitrogen atom occurs. The possibility of the direct introduction of nitrogen-containing nucleophiles into the side chain of pyrylium salts was demonstrated in the case of the reactions of ethynyl-substituted pyrylium salts. Such monoiminium salts were previously synthesized by the reaction of ethoxyvinyl derivatives of pyrylium salts with primary amines [6] or by condensation of salts that contain an active methyl group with DMF in acetic anhydride [7]. In reactions with ethynyl-substituted pyrylium salts ammonium acetate and methyl-, butyl-, and benzylamine attack the α position of the pyrylium cation and form the difficult-to-obtain pyridines XXIV-XXVII and pyridinium salts XXVIII-XXX, with the ethynyl substituent in the 4 position of the heteroring retained.

Addition of methylamine to the triple bond and replacement of the ring oxygen atom by a nitrogen atom also occur when gaseous methylamine is passed into a solution of salt IIIa in acetonitrile. We assume that methylamine initially attacks the α-carbon atom of the pyrylium ring, after which the nucleophile adds to the β-carbon atom of the triple bond.



III d R=CH_3, Ar=$C_6H_4OCH_3$-*p*; XXVIII R^1=CH_3, XXIX R^1=C_4H_9, XXX R^1=CH_2Ph

This reaction is confirmed by the reaction of equimolar amounts of methylamine and perchlorate IIIa, which leads to the formation of XXVIII rather than a mixture of products XXVIII and XXXI. Salt XXVIII can react with a new portion of methylamine at the triple bond to form pyridinium perchlorate XXXI.

According to the results obtained the properties that are typical for both a triple bond and for a pyrylium ring are retained in stable ethynyl carbonium ions such as 4-phenyl-

ethynyl pyrylium ions. In addition, the mutual effect of the two fragments in this saltlike class of compounds advantageously changes their behavior with respect to nucleophilic reagents, i.e., the ethynyl group becomes more active, and the pyrylium ring becomes more selective. This opens up the possibility of directing the reaction of 4-ethynylpyrylium salts with nucleophiles along one of three pathways: addition to the ethynyl group with retention of the pyrylium ring, transformation of the latter without a change in the C≡C bond, and simultaneous addition of the nucleophile to the two reaction centers. Diverse pyrylium and pyridinium derivatives, as well as uncharged oxygen- and nitrogen-containing heterocycles with unsaturated and functional substituents, that are difficult to obtain and are valuable in a practical respect can thus be synthesized.

EXPERIMENTAL

The IR spectra of thin layers of suspensions of the compounds in mineral oil (NaCl prism) were recorded with a Specord IR-75 spectrometer. The PMR spectra were obtained with a Tesla BS-487 spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The molecular masses were determined with a Finnigan 4021 chromatographic mass spectrometer (70 eV).

The characteristics of IX-XVII are presented in Tables 1 and 2.

The results of elementary analysis for C, H, Cl, and N were in agreement with the calculated values.

Perchlorates IIIa-c were synthesized by the methods in [8-10].

We used similar methods to obtain 2,6-diphenyl-3-methyl-4-phenylethynylpyrylium perchlorate (I, $C_{26}H_{19}ClO_5$), with mp 211-212°C (from CH_3CN), in 53% yield. IR spectrum (C≡C), 1614, 1594 (C=C), 1100 cm^{-1} (ClO_4^-). PMR spectrum (CF_3COOH): 2.37 (3H, s, CH_3), 6.95-8.05 ppm (16H, m, Ar). We also used similar methods to obtain 2,6-di(p-methoxyphenyl)-4-phenylethynylpyrylium perchlorate (IIId, $C_{29}H_{25}ClO_7$), with mp 234-235°C (from CH_3CN), in 66% yield. IR spectrum: 2207 (C≡C), 1615, 1605, 1514 (C=C), 1267 (C-O-C), 1100 cm^{-1} (ClO_4^-). PMR spectrum (CF_3COOH): 2.45 (6H, s, $2CH_3$), 3.57 (6H, s, $2OCH_3$), 6.7-7.75 ppm (13H, m, Ar).

2,6-Diphenyl-3-methyl-4-[1'-(2", 6"-diphenyl-3"-methyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyrylium Perchlorate (II, $C_{52}H_{39}ClO_7$). A 1.34-g (3 mmole) sample of perchlorate I was refluxed in 25 ml of ethanol for 0.5 h, after which the mixture was cooled and filtered to give 1.45 g (60%) of a dark-violet precipitate with mp 205°C [from isopropyl alcohol-acetonitrile (2:1)]. IR spectrum: 1640 (C=O), 1607, 1594, 1570 (C=C), 1260 (C-O-C), 1100 cm^{-1} (ClO_4^-). PMR spectrum (CF_3COOH): 1.7-2.47 (6H, m, $2CH_3$), 6.65-7.96 ppm (33H, m, 1H, CH, 1H pyran proton, 31H, Ar).

2,6-diphenyl-3,5-dimethyl-4-(β-ethoxy)styrylpyrylium Perchlorate (IVb, $C_{29}H_{27}ClO_6$). A suspension of 1.84 g (4 mmole) of perchlorate IIIa in 20 ml of ethanol was refluxed for 0.5 h, after which it was cooled and filtered to give 1.68 g (83%) of a yellow precipitate with mp 230-231°C (from CH_3CN). IR spectrum: 1610, 1590, 1530 (C=C), 1270 (C-O-C), 1100 cm^{-1} (ClO_4^-). PMR spectrum (CH_3NO_2): 1.55 (3H, t, CH_2CH_3), 2.37 (6H, s, $2CH_3$), 6.25 (1H, s, =CH), 7.4-7.92 ppm (15H, m, Ar). PMR spectrum ($C_6H_5NO_2$): 1.56 (3H, t, CH_2CH_3), 2.52 (6H, s, $2CH_3$), 4.37 ppm (2H, q, CH_2CH_3).

A similar procedure was used to obtain 2,6-diphenyl-3,5-dimethyl-4-(β-methoxyl)styrylpyrylium perchlorate (IVa, $C_{28}H_{25}ClO_6$) [mp 192-193°C [from methanol-acetonitrile (2:1)], 86% yield. IR spectrum: 1610, 1580, 1550 (C=C), 1240 (C-O-C), 1100 cm^{-1} (ClO_4^-). PMR spectrum ($CDCl_3$): 2.05 (6H, s, $2CH_3$), 4.0 (3H, s, OCH_3), 6.01 (1H, s, CH), 7.1-7.86 ppm (15H, m, Ar)] and 2,6-diphenyl-3,5-dimethyl-4-(β-isopropoxyl)styrylpyrylium perchlorate (IVc, $C_{30}H_{29}ClO_6$) [mp 158°C [from isopropyl alcohol-acetonitrile (5:1)]. IR spectrum: 1600, 1580, 1547, 1514 (C=C), 1234 (C-O-C), 1100 cm^{-1} (ClO_4^-)].

2,6-Diphenyl-3,5-dimethyl-4-phenacylpyrylium Perchlorate (V, $C_{27}H_{23}ClO_6$). A 5-ml sample of CF_3COOH was added to 0.5 g (1 mmole) of perchlorate IVb, and the mixture was allowed to stand at 22°C for 0.5 h. Dilution of the reaction mixture with ether (30-40 ml) gave 0.46 g (98%) of a yellow precipitate with mp 225-226°C (from CH_3COOH). IR spectrum: 1680 (C=O), 1614, 1600, 1574 (C=C), 1100 cm^{-1} (ClO_4^-). PMR spectrum ($CDCl_3$): 2.45 (6H, s, $2CH_3$), 5.0 (2H, s, CH_2), 7.3-8.17 ppm (15H, m, Ar).

2,6-Diphenyl-3,5-dimethyl-4-benzoylmethylenepyran (VI, $C_{27}H_{22}O_2$). A 5-ml sample of 10% NaOH solution was added to a suspension of 0.47 g (1 mmole) of perchlorate V in 10 ml of diethyl ether, and the mixture was stirred until the solid material had disappeared. The

ether layer was separated, washed with water, and evaporated, and the residue was recrystallized from isopropyl alcohol to give 0.3 g (81%) of a product with mp 158-159°C. IR spectrum: 1647 (C=O), 1620, 1600, 1534 (C=C), 1247, 1214 cm^{-1} (C–O–C). PMR spectrum ($CDCl_3$): 2.0 (6H, s, $2CH_3$), 6.3 (1H, s, =CH), 7.12-8.12 ppm (15H, m, Ar).

2,6-Diphenyl-3,5-dimethyl-4-[1'-(2",6"-diphenyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyrylium Perchlorate (VII, $C_{52}H_{39}ClO_7$). A mixture of 0.21 g (0.5 mmole) of 2,6-diphenyl-4-phenylethynylpyrylium perchlorate and 0.37 g (1 mmole) of pyran VI in 5 ml of absolute acetonitrile was refluxed for 6 h, after which it was diluted with ether (50 ml) and filtered to give 0.39 g (97%) of a dark-violet precipitate with mp 199-200°C [from isopropyl alcohol–acetonitrile (2:1)]. IR spectrum: 1634 (C=O), 1600, 1580, 1560 (C=C), 1267 (C–O–C), 1100 cm^{-1} (ClO_4^-). PMR spectrum ($CDCl_3$): 2.36 (6H, s, $2CH_3$), 6.25-8.17 ppm (33H, m, 1H, CH, 2H pyran protons, 30H, Ar).

2,6-Diphenyl-3,5-dimethyl-4-[1'-(2",6"-diphenyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyridine (VIII, $C_{52}H_{39}NO_2$). A stream of dry ammonia was passed for 10 min into a suspension of 0.2 g (0.25 mmole) of perchlorate VII in absolute benzene, after which the benzene solution was evaporated, and the residue was recrystallized from isopropyl alcohol–acetonitrile (2:1) to give 0.07 g (41%) of a product with mp 208-209°C. IR spectrum: 1647 (C=O), 1594, 1574, 1540 (C=C), 1234 cm^{-1} (C–O–C). PMR spectrum ($CDCl_3$): 2.27 (6H, s, $2CH_3$), 6.0 (2H, s, pyran protons), 6.32 (1H, s, =CH), 7.07-7.77 ppm (30 H, m, Ar).

4-Aminostyrylpyrylium Perchlorates IX-XV. An equimolar amount of the corresponding amine dissolved in absolute acetonitrile was added dropwise with stirring and cooling (-5°C) to a suspension of 2 mmole of 4-phenylethynylpyrylium perchlorate IIIa-c in absolute acetonitrile, and the mixture was stirred. It was then diluted with ether, and the precipitated aminostyrylpyrylium salt was removed by filtration and crystallized from isopropyl alcohol with the addition of acetonitrile.

Pyranylideneiminoethanes XVI-XIX. An equimolar amount of absolute triethylamine was added to a suspension of 1 mmole of 4-aminostyrylpyrylium perchlorate IX-XII in 10 ml of absolute benzene, and the mixture was stirred until the characteristic color of the pyrylium salt vanished. The mixture was then diluted with 20-30 ml of water, and the benzene layer was separated, washed with water, and evaporated. The residue was recrystallized from benzene–hexane (1:5).

Phenacylpyridines XX-XXII. A mixture of 4-aminostyrylpyrylium perchlorate IX, X, or XII and a tenfold excess of ammonium acetate was refluxed in acetic acid for 1 h, after which it was diluted with water and extracted with benzene. The benzene extracts were washed with water to pH 7 and evaporated, and the residue was crystallized from isopropyl alcohol-acetonitrile (3:1).

2,6-Diphenyl-4-benzoylmethylenepyran (XXIII, $C_{25}H_{18}O_2$). A 5-ml sample of CF_3COOH was added to 0.52 g (1 mmole) of 2,6-diphenyl-4-(β-phenylamino)styrylpyrylium perchlorate (IX), and the mixture was allowed to stand at 22°C for 90 h. It was then diluted with 20 ml of water and extracted with ether. The ether extracts were washed with weak alkali solution (5%) and then with water to pH 7 and evaporated. The residue was crystallized from isopropyl alcohol to give 0.25 g (71%) of a product with mp 159-160°C (mp 160°C [11]). IR spectrum: 1654 (C=O), 1607, 1580, 1514 (C=C), 1273, 1207 cm^{-1} (C–O–C). PMR spectrum ($CDCl_3$): 6.2 (1H, s, pyran proton), 6.42 (1H, s, =CH), 7.0-7.95 (15H, m, Ar), 8.62 ppm (1H, s, pyran proton).

2,6-Diphenyl-3,5-dimthyl-4-benzoylmethylenepyran (VI). A 5-ml sample of CF_3COOH was added to 0.55 g (1 mmole) of 2,6-diphenyl-3,5-dimethyl-4-(β-phenylamino)styrylpyrylium perchlorate (XII), and the mixture was allowed to stand at 22°C for 40 h. The product was isolated in the same way as XIII. The physicochemical characteristics were in agreement with the constants of benzoylmethylenepyran obtained from perchlorate V.

4-Phenylethynylpyridines XXIV-XXVII. A mixture of perchlorate IIIa-d and a tenfold excess of ammonium acetate was refluxed in acetic acid until the color of the salt vanished in the course of 0.5-1 h, after which the mixture was diluted with water and extracted with benzene. The benzene extracts were washed with water to pH 7 and evaporated. 2,6-Diphenyl-[di(p-methoxyphenyl)]-3,5-dimethyl-4-phenylethynylpyridines XXVI and XXVII were crystallized from isopropyl alcohol. 2,6-Diphenyl[di(p-methoxyphenyl)]-4-phenylethynylpyridines XXIV and XXV were purified by chromatography with a column packed with Al_2O_3 by elution with benzene (R_f of XXIV 0.8, R_f of XXV 0.9); after removal of the solvent, the residue was recrystallized from isopropyl alcohol.

1-Methyl-2,6-diphenyl-3,5-dimethyl-4-phenylethynyl-pyridinium Perchlorate (XXVIII, $C_{28}H_{24}ClNO_4$). A 0.162-g (2.4 mmole) sample of methylamine hydrochloride was added to a suspension of 0.92 g (2 mmole) of perchlorate IIIa in 15 ml of absolute ethanol, after which a solution of 3.14 ml of sodium ethoxide prepared from 0.07 g of sodium in 4 ml of absolute ethanol was added dropwise, and the reaction mixture was refluxed until the solid material had dissolved. After hot filtration, 0.5 g (53%) of a light-yellow precipitate with mp 237-238°C (from isopropyl alcohol) crystallized from the ethanol. IR spectrum: 2225 (C≡C), 1600, 1590 (C=C), 1100 cm^{-1} (ClO_4^-). PMR spectrum (CF_3COOH): 2.02 (6H, s, $2CH_3$), 3.2 (3H, s, CH_3), 6.87-7.42 ppm (16H, m, Ar).

1-Butyl-2,6-diphenyl-3,5-dimethyl-4-phenylethynyl-pyridinium Perchlorate (XXIX, $C_{31}H_{30}ClNO_4$). This compound was obtained from 0.46 g (1 mmole) of perchlorate IIIa and 0.13 g (1.2 mmole) of butylamine hydrochloride as in the preparation of XXVIII. Workup gave 0.4 g (78%) of a product with mp 281-282°C. IR spectrum: 2200 (C≡C), 1605, 1585 (C=C), 1100 cm^{-1} (ClO_4^-).

1-Benzyl-2,6-diphenyl-3,5-dimethyl-4-phenylethynyl-pyridinium Perchlorate (XXX, $C_{34}H_{28}ClNO_4$). A solution of 0.24 ml (2 mmole) of benzylamine in 2 ml of absolute acetonitrile was added dropwise with stirring and cooling with ice water to a suspension of 0.92 g (2 mmole) of perchlorate IIIa in 8 ml of absolute acetonitrile, and the mixture was stirred at room temperature for 0.5 h. Dilution of the reaction mixture with ether (50 ml) gave 0.95 g (87%) of a light-yellow precipitate with mp 237°C (from CH_3COOH). IR spectrum: 2225 (C≡C), 1600, 1570 (C=C), 1100 cm^{-1} (ClO_4^-). PMR spectrum ($CDCl_3$): 2.3 (6H, s, $2CH_3$), 5.42 (2H, s, CH_2), 6.37-8.0 ppm (20H, m, Ar).

1-Methyl-2,6-diphenyl-3,5-dimethyl-4-(β-methylamino)-styrylpyridinium Perchlorate (XXXI, $C_{29}H_{28}ClN_2O_4$). A stream of dry methylamine was passed into a suspension of 1.84 g (4 mmole) of perchlorate IIIa in 15 ml of absolute acetonitrile until the starting pyrylium salt had dissolved (1-2 min). Dilution of the reaction mass gave 1.95 g (97%) of a yellow precipitate with mp 244-245°C [from ethyl acetate–acetonitrile (6:1)]. IR spectrum: 3367 (NH), 1614, 1600, 1574 (C=C), 1100 cm^{-1} (ClO_4^-). PMR spectrum (d_7-DMF): 1.73 (6H, s, $2CH_3$), 3.36 (3H, s, pyridinium NCH_3), 5.3 (1H, s, =CH), 6.9 (1H, broad s, NH), 7.17-7.8 ppm (15H, m, Ar). PMR spectrum ($C_6H_5NO_2$): 1.82 (6H, s, $2CH_3$), 2.88 (3H, d, aminovinyl NCH_3), 5.17 ppm (1H, s, =CH).

1-Methyl-2,6-diphenyl-3,5-dimethyl-4-phenacylpyridinium Perchlorate (XXXII, $C_{28}H_{26}ClNO_5$). A 2-ml sample of CF_3COOH was added to 0.5 g (1 mmole) of perchlorate XXXI, after which the mixture was stirred until the solid had dissolved. The solution was diluted with water and extracted with chloroform. The extracts were washed with water and evaporated, and the residue was recrystallized from isopropyl alcohol and acetic acid to give 0.35 g (71%) of a product with mp 142°C. IR spectrum: 1687 (C=O), 1600, 1580 (C=C), 1273, 1220 (C–O–C), 1100 cm^{-1} (ClO_4^-). PMR spectrum ($CDCl_3$): 2.03 (6H, s, $2CH_3$), 3.5 (3H, s, NCH_3), 4.77 (2H, s, CH_2), 7.05-8.15 ppm (15H, m, Ar).

LITERATURE CITED

1. A. V. Koblik, L. A. Murad'yan, O. E. Kompan, D. S. Yufit, Yu. T. Struchkov, Yu. A. Zhdanov, L. P. Olekhnovich, and G. P. Zolotovskova, Khim. Geterotsikl. Soedin., No. 7, 885 (1988).
2. M. Siemiatycki, Ann. Chim., No. 2, 189 (1957).
3. M. Basseti and B. Floris, Summaries of Papers Presented at the 6th European Conference on Organometallic Chemistry [Russian translation], Riga (1985), p. 118.
4. R. D. Bach, R. A. Woodward, Y. J. Anderson, and M. D. Glick, J. Org. Chem., 47, 3707 (1982).
5. A. T. Balaban, A. Dinculescu, G. N. Dorofeenko, G. W. Fischer, A. V. Koblik, V. V. Mezheritskii, and W. Schroth, Advances in Heterocyclic Chemistry, Supplement 2, Academic Press, New York (1982), p. 323.
6. G. N. Dorofeenko, V. V. Mezheritskii, and A. L. Vasserman, Khim. Geterotsikl. Soedin., No. 10, 1338 (1974).
7. G. A. Reynolds and J. A. Van Allan, J. Org. Chem., 34, 2736 (1969).
8. G. N. Dorofeenko, A. V. Koblik, L. A. Murad'yan, T. I. Polyakova, and B. A. Tertov, Zh. Org. Khim., 16, 1741 (1980).
9. A. V. Koblik, L. A. Murad'yan, S. G. Blagorodov, L. N. Chernavskaya, and N. A. Dmitrieva, USSR Author's Certificate No. 1189861; Byull. Izobret., No. 41, 103 (1985).

10. N. A. Dmitrieva, L. N. Chernavskaya, S. G. Blagorodov, A. P. Shepelev, A. V. Koblik, and L. A. Murad'yan, USSR Author's Certificate No. 1244148; Byull. Izobret., No. 26, 104 (1986).
11. H. Strzelecka and M. M. Simalty-Siemiatycki, Compt. Rend., C, 260, no. 14, 3989 (1965).

ETHYNYL CARBONIUM IONS.

3.* DIENE SYNTHESIS WITH 4-PHENYLETHYNYLPYRYLIUM SALTS

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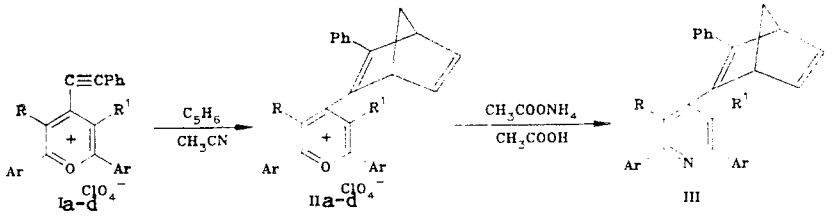
Norbornadiene derivatives of pyrylium salts were obtained for the first time by [4 + 2] cycloaddition of cyclopentadienes and 2,6-diaryl-4-phenylethynylpyrylium salts with and without methyl groups in the 3 and 5 positions. Their photochemical transformations were studied.

The synthesis developed by us [2] of 4-phenylethynylpyrylium salts that contain an activated (by the electron-acceptor pyrylium cation) C≡C bond for the first time opened up the possibility of introducing a labile carbocyclic group such as a norbornadienyl group into a charged heteroring. These molecules could become a convenient model in the study of processes involving the accumulation and utilization of the energy of visible light.

To obtain 4-norbornadienylpyrylium salts we set out to construct a carbocycle on an unsaturated substituent in the pyrylium cation using the Diels–Alder reaction.

We showed that refluxing 2,6-diphenyl-, 2,6-di(p-methoxyphenyl)-, 2,6-diphenyl-3-methyl-, and 2,6-diphenyl-3,5-dimethyl-4-phenylethynylpyrylium perchlorates Ia-d with cyclopentadiene in absolute acetonitrile leads to the formation of 2,6-diphenyl[di(p-methoxyphenyl)]-4-(2'-phenyl-3'-norbornadienyl)pyrylium and 2,6-diphenyl-3-methyl(3,5-dimethyl)-4-(2'-phenyl-3'-norbornadienyl)pyrylium perchlorates IIa-d in high yields (Table 1); the formation of other products of addition to the triple bond was not noted.



I, IIa,c,d Ar = Ph, b Ar = *p*-$OCH_3C_6H_4$; a,b R = H; c,d R = CH_3; a-c R^1 = H, d R^1 = CH_3;
III Ar = Ph, R = CH_3, R^1 = H

The results of cycloaddition provide evidence that the charge in 4-norbornadienylpyrylium salts Ia-d is concentrated primarily in the pyrylium ring, while the unsaturated substituent retains the properties of a triple bond, i.e., 4-norbornadienylpyrylium salts are ethynyl carbonium ions rather than allenyl cations, for which [2 + 2]-cycloaddition reactions are generally characteristic on reaction with cyclopentadiene [3-5].

Pentamethylcyclopentadiene is also capable of reacting with 4-ethynyl-substituted pyrylium salts. Using this method we were able to synthesize 2,6-di(p-methoxyphenyl)-4-(2'-phenyl-1',4',5',6',7'-pentamethyl-7'H-3'-norbornadienyl)pyrylium perchlorate (IIa). However,

*See [1] for Communication 2.

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