ETHYNYL CARBONIUM IONS.

1. REACTION OF 2,6-DIARYL-4-PHENYLETHYNYLPYRULIUM PERCHLORATES WITH OXYGEN-CONTAINING NUCLEOPHILES

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UDC 547.814.5'821.3:543.422.25:548.737

When 2,6-diaryl-4-phenylethynylpyrylium perchlorates are refluxed in water, methanol, or ethanol, they are converted to monomethinecyanines, the formation of which is explained by hydration of the phenylethynyl group and subsequent [2 + 2]-cycloaddition of the resulting 2,6-diaryl-4-benzoylmethylenepyrans to the starting pyrylium salt. The corresponding pyridine derivatives were obtained by the action of ammonia and aniline on the monomethinecyanines. The IR and PMR spectra of the compounds and the results of x-ray diffraction analysis of 2,6-diphenyl-4-[1'-(2",6"-diphenyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyridine are presented.

Activation of the C≡C bond substantially enriches the synthetic possibilities of acetylenes in addition reactions and processes involving the formation of carbo- and heterocycles [1]. Extremely promising in this respect is the use of ethynylcarbonium ions, the properties of which, however, have been little studied because of the difficulty involved in obtaining them and their high activities [2]. The known cations of this type behave basically like ambident allenyl ions [3], while we were interested in charged systems in which the nature of the C≡C bond would be retained.

To solve this problem we attempted to unite in one structure the ethynyl fragment and a stable carbonium ion. The well-studied carboxonium ions best fill the role of the latter [4]. The 4-phenylethynylpyrylium salts that we obtained [5, 6] are the first of such systems. Characteristic absorption bands of both a pyrylium cation and a C≡C bond (2200 cm^{-1}) show up distinctly in their IR spectra. This system opens up the possibility of introducing a nucleophile not only in the pyrylium ring but also in the hydrocarbon substituent attached to it; on the other hand, in addition to the addition of nucleophiles, the activated ethynyl group can be involved in the recyclization processes that are characteristic for pyrylium salts [7].

We commenced our investigations of the properties of stable ethynyl carbonium ions in the case of 2,6-diaryl-4-phenylethynylpyrylium salts Ia, b with a study of their reactions with oxygen-containing nucleophiles. We expected the formation of difficult-to-obtain 4-phenacylpyrylium salts, which could take place both via classical hydration of acetylenes and via the addition of the nucleophile in the α position of the pyrylium ring and subsequent recyclization with inclusion of the phenylethynyl group into a ring.

When we refluxed 2,6-diphenyl-4-phenylethynylpyrylium perchlorate (Ia) in water, methanol, and ethanol, we obtained deeply colored blue-violet precipitates, the IR spectra of which contained absorption bands of a pyrylium perchlorate (1580, 1610, 1100 cm^{-1}) but did not contain absorption bands of a C≡C bond. Since we were unable to obtain all three products in the analytically pure state, they were treated with ammonia [the typical (for pyrylium salts) method of identification by conversion to pyridine derivatives [7]]. In all three cases we isolated orange-red crystals, the IR spectra and melting points of which coincided. Thus all three blue-violet precipitates were the same substance, which under the influence of ammonia gives a nitrogen-containing product with the empirical formula $C_{50}H_{35}NO_2$ (according

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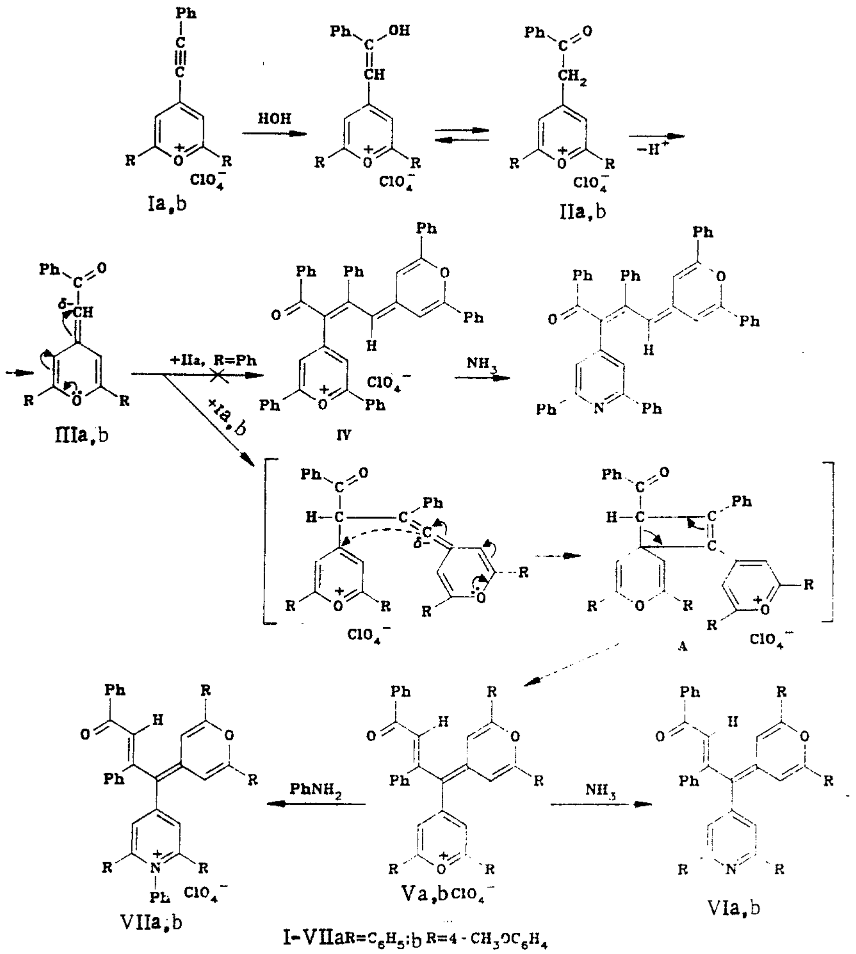
0009-3122/88/2407-0725$12.50

to the results of elementary analysis and mass-spectrometric determination of the molecular mass).

On the basis of this one might have concluded that salt Ia reacts with oxygen-containing nucleophiles to give trimethinecyanine IV, which was then converted to a pyridine derivative. In the IR spectrum of the latter we observed an absorption band of a conjugated carbonyl group (1660 cm^{-1}), but the PMR spectrum was uninformative (weak-field multiplet signal at δ 6.8-8.0 ppm). To establish the structure of the nitrogen-containing compound we therefore subjected it to x-ray diffraction analysis, which showed that this compound is 2,6-diphenyl-4-[1'-(2",6"-diphenyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyridine. Consequently, the colored precipitates isolated from the reaction mixtures of starting salt Ia with O-nucleophiles are not a trimethinecyanine but rather monomethinecyanine Va, which is formed via the scheme



I-VIIa R=C_6H_5; b R=4-$CH_3OC_6H_4$

Salt Ia is converted to benzoylmethylenepyran IIIa, which undergoes [2 + 2]-cycloaddition with starting perchlorate Ia; for the sake of clarity this reaction can be depicted as two nucleophilic attacks, first, by the CH group of the methylenepyran at the activated triple bond and, second, by the sp-hybridized carbon atom of the resulting allene grouping at the γ position of the pyrylium cation to which starting methylenepyran IIIA was converted. Cyclobutene derivative A is converted to diene Va (cf. [1], p. 241). It is apparent that the presence of water is necessary for this transformation; however, we observed that the reaction proceeds faster in nonanhydrous alcohols than in pure water.

The structure of the VIa molecule and the bond lengths are presented in Fig. 1, the bond angles are presented in Table 1, and the coordinates of the nonhydrogen atoms are given in Table 2. The pyranyl and pyridine fragments have the usual geometries [8-10]. The angle of 33.5° between the planes of the heterorings does not rid this part of the molecule of steric overload, as evidenced by both the rather short intramolecular $C_{(2)}\ldots C_{(22)}$ [3.106(7) Å] and $C_{(2)}\ldots C_{(23)}$ [3.067 Å] distances and the distortion of the angles at the $C_{(18)}$ atom and the exocyclic angles at the $C_{(3)}$ and $C_{(23)}$ atoms: $C_{(2)}C_{(3)}C_{(18)}$ 123.6(4)°, $C_{(4)}C_{(3)}C_{(18)}$ 120.0(4)°, $C_{(3)}C_{(18)}C_{(19)}$ 114.4(4)°, $C_{(3)}C_{(18)}C_{(23)}$ 125.4(4)°, $C_{(19)}C_{(18)}C_{(23)}$ 120.1(4)°,

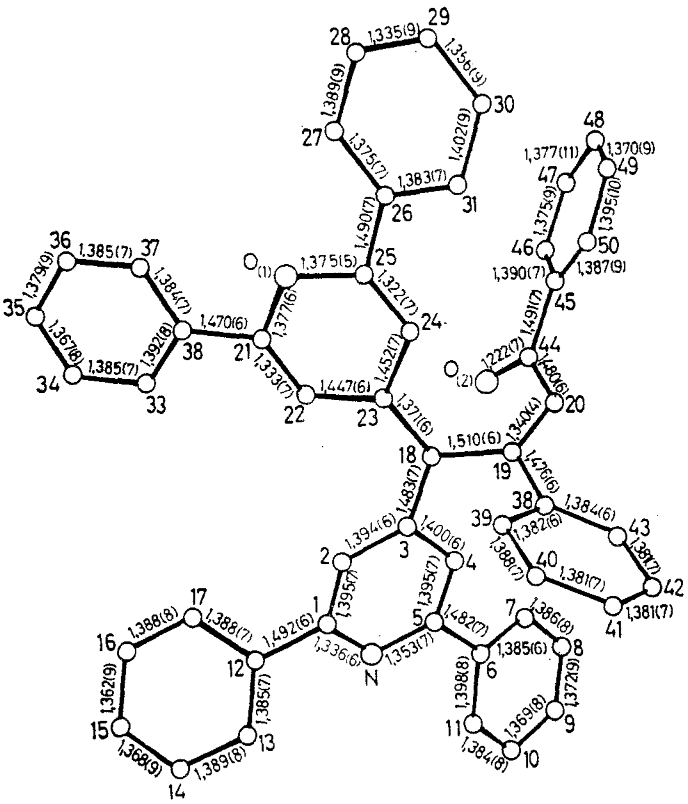


Fig. 1. Structure of the pyridine VIa molecule in the crystal.

TABLE 1. Bond Angles (ω) in the VIa Molecule

Angle	ω°	Angle	ω°	Angle	ω°
$C_{(1)}NC_{(5)}$	117,4(4)	$C_{(3)}C_{(18)}C_{(19)}$	114,4(4)	$C_{(21)}C_{(22)}C_{(23)}$	121,7(4)
$NC_{(1)}C_{(2)}$	123,7(4)	$C_{(3)}C_{(18)}C_{(23)}$	125,4(4)	$C_{(21)}C_{(32)}C_{(37)}$	120,9(4)
$NC_{(1)}C_{(12)}$	116.3(4)	$C_{(19)}C_{(18)}C_{(23)}$	120.1(4)	$C_{(33)}C_{(32)}C_{(37)}$	117,4(4)
$C_{(2)}C_{(1)}C_{(12)}$	120,0(4)	$C_{(18)}C_{(19)}C_{(20)}$	122,1(4)	$C_{(32)}C_{(33)}C_{(34)}$	121,1(5)
$C_{(1)}C_{(2)}C_{(3)}$	119,4(4)	$C_{(18)}C_{(19)}C_{(38)}$	116,1(4)	$C_{(33)}C_{(34)}C_{(35)}$	120,4(5)
$C_{(2)}C_{(3)}C_{(4)}$	117,0(4)	$C_{(20)}C_{(19)}C_{(38)}$	121,6(4)	$C_{(34)}C_{(35)}C_{(36)}$	119,4(5)
$C_{(2)}C_{(3)}C_{(18)}$	123.0(4)	$C_{(19)}C_{(20)}C_{(44)}$	124,3(4)	$C_{(35)}C_{(36)}C_{(37)}$	120,5(5)
$C_{(4)}C_{(3)}C_{(18)}$	120,0(4)	$C_{(21)}O_{(1)}C_{(25)}$	118,1(4)	$C_{(38)}C_{(37)}C_{(36)}$	121,1(5)
$C_{(3)}C_{(4)}C_{(5)}$	120,0(4)	$O_{(1)}C_{(21)}C_{(22)}$	121,9(4)	$C_{(19)}C_{(38)}C_{(39)}$	120,0(4)
$NC_{(5)}C_{(4)}$	122,4(4)	$O_{(1)}C_{(21)}C_{(32)}$	111,1(4)	$C_{(19)}C_{(38)}C_{(43)}$	121,3(4)
$NC_{(5)}C_{(6)}$	116,3(4)	$C_{(22)}C_{(23)}C_{(32)}$	126,9(4)	$C_{(39)}C_{(38)}C_{(43)}$	118,6(4)
$C_{(4)}C_{(5)}C_{(6)}$	121,2(4)	$C_{(21)}C_{(22)}C_{(23)}$	122,0(4)	$C_{(38)}C_{(39)}C_{(40)}$	120,3(5)
$C_{(5)}C_{(6)}C_{(7)}$	122,0(4)	$C_{(18)}C_{(23)}C_{(22)}$	125,1(4)	$C_{(39)}C_{(40)}C_{(41)}$	120,2(5)
$C_{(5)}C_{(6)}C_{(11)}$	119,7(4)	$C_{(18)}C_{(23)}C_{(24)}$	121,6(4)	$C_{(40)}C_{(41)}C_{(42)}$	119,8(6)
$C_{(7)}C_{(6)}C_{(11)}$	118,2(4)	$C_{(22)}C_{(23)}C_{(24)}$	113,3(4)	$C_{(41)}C_{(42)}C_{(43)}$	119,8(5)
$C_{(6)}C_{(7)}C_{(8)}$	121,3(5)	$C_{(23)}C_{(24)}C_{(25)}$	121,9(4)	$C_{(38)}C_{(43)}C_{(42)}$	121,2(5)
$C_{(7)}C_{(8)}C_{(9)}$	119,2(5)	$OC_{(25)}C_{(24)}$	122,5(4)	$O_{(2)}C_{(44)}C_{(20)}$	121,8(4)
$C_{(8)}C_{(9)}C_{(10)}$	120,7(6)	$OC_{(25)}C_{(26)}$	110,3(4)	$O_{(2)}C_{(44)}C_{(45)}$	119,6(4)
$C_{(9)}C_{(10)}C_{(11)}$	120,3(6)	$C_{(24)}C_{(25)}C_{(26)}$	127,1(4)	$C_{(20)}C_{(44)}C_{(45)}$	118,6(4)
$C_{(6)}C_{(11)}C_{(10)}$	120,2(5)	$C_{(25)}C_{(26)}C_{(27)}$	121,4(4)	$C_{(44)}C_{(45)}C_{(46)}$	118,6(4)
$C_{(1)}C_{(12)}C_{(13)}$	121,4(4)	$C_{(25)}C_{(26)}C_{(31)}$	119.9(4)	$C_{(44)}C_{(45)}C_{(50)}$	121.2(5)
$C_{(1)}C_{(12)}C_{(17)}$	120,0(4)	$C_{(27)}C_{(26)}C_{(31)}$	118,8(5)	$C_{(46)}C_{(45)}C_{(50)}$	120,0(5)
$C_{(13)}C_{(12)}C_{(17)}$	118,6(4)	$C_{(26)}C_{(27)}C_{(28)}$	119.8(5)	$C_{(45)}C_{(46)}C_{(47)}$	120,2(5)
$C_{(12)}C_{(13)}C_{(14)}$	120,4(5)	$C_{(27)}C_{(28)}C_{(29)}$	121,5(6)	$C_{(46)}C_{(47)}C_{(48)}$	119,7(6)
$C_{(13)}C_{(14)}C_{(15)}$	120,2(6)	$C_{(28)}C_{(29)}C_{(30)}$	120,0(6)	$C_{(47)}C_{(48)}C_{(49)}$	120,7(6)
$C_{(14)}C_{(15)}C_{(16)}$	120,0(6)	$C_{(29)}C_{(30)}C_{(31)}$	120,3(6)	$C_{(48)}C_{(49)}C_{(50)}$	120,3(6)
$C_{(15)}C_{(16)}C_{(17)}$	120,6(6)	$C_{(26)}C_{(31)}C_{(30)}$	119,6(5)	$C_{(45)}C_{(50)}C_{(49)}$	118,9(6)
$C_{(12)}C_{(17)}C_{(16)}$	120,0(5)				

$C_{(18)}C_{(23)}C_{(22)}$ 125.1(4)°, $C_{(18)}C_{(23)}C_{(24)}$ 121.6(4)°. A large degree of rotation of the pyridine ring relative to the pyranyl ring and the $C_{(18)}$ and $C_{(19)}$ atoms, which lie in the same plane, would promote a decrease in the steric strain. However, conjugation in the pyranyl—$C_{(18)}$—pyridine system, as evidenced by the lengthening, although very slight, of the $C_{(18)}=C_{(23)}$ double bond to 1.371(6)° Å.

TABLE 2. Coordinates of the Nonhydrogen Atoms ($\times 10^4$) in VIa

Atom	x	y	z	Atom	x	y	z
$O_{(1)}$	3638(3)	5648(2)	565(2)	$C_{(25)}$	4588(4)	5728(3)	1334(3)
$O_{(2)}$	6160(4)	9316(3)	4158(3)	$C_{(26)}$	4101(4)	4764(3)	1441(3)
N	8763(4)	11069(2)	1908(3)	$C_{(27)}$	2734(5)	4062(4)	997(4)
$C_{(1)}$	8004(4)	10113(3)	1114(3)	$C_{(28)}$	2306(5)	3189(4)	1137(4)
$C_{(2)}$	7494(4)	9204(3)	1197(3)	$C_{(29)}$	3191(6)	3013(4)	1704(4)
$C_{(3)}$	7742(4)	9281(3)	2158(3)	$C_{(30)}$	4552(6)	3680(4)	2134(5)
$C_{(4)}$	8535(4)	10282(3)	2992(3)	$C_{(31)}$	5030(5)	4568(4)	2006(4)
$C_{(5)}$	9032(4)	11149(3)	2841(3)	$C_{(32)}$	2706(4)	6317(3)	−387(3)
$C_{(6)}$	9861(4)	12221(3)	3711(3)	$C_{(33)}$	2703(5)	7072(3)	−679(4)
$C_{(7)}$	9738(5)	12528(3)	4710(4)	$C_{(34)}$	1647(5)	6862(4)	−1473(4)
$C_{(8)}$	10478(6)	13546(4)	5510(4)	$C_{(35)}$	574(5)	5904(4)	−1983(4)
$C_{(9)}$	11363(6)	14261(4)	5308(4)	$C_{(36)}$	537(5)	5159(4)	−1690(4)
$C_{(10)}$	11514(6)	13978(4)	4329(4)	$C_{(37)}$	1595(5)	5360(3)	−903(4)
$C_{(11)}$	10764(5)	12965(4)	3526(4)	$C_{(38)}$	9619(4)	8237(3)	2918(3)
$C_{(12)}$	7692(4)	10051(3)	98(3)	$C_{(39)}$	9665(4)	7561(3)	1927(4)
$C_{(13)}$	8740(5)	10438(4)	−243(4)	$C_{(40)}$	10922(5)	7378(4)	1716(4)
$C_{(14)}$	8435(6)	9910(4)	−1203(4)	$C_{(41)}$	12133(5)	7863(4)	2496(4)
$C_{(15)}$	7081(6)	9454(4)	−1804(4)	$C_{(42)}$	12108(5)	8560(4)	3475(4)
$C_{(16)}$	6033(6)	9498(4)	−1470(4)	$C_{(43)}$	10852(5)	8732(4)	3685(4)
$C_{(17)}$	6330(5)	8353(3)	−532(4)	$C_{(44)}$	6612(5)	8709(3)	4322(3)
$C_{(18)}$	7263(4)	8391(3)	2314(3)	$C_{(45)}$	5856(4)	8184(4)	4858(3)
$C_{(19)}$	8264(4)	8391(3)	3147(3)	$C_{(46)}$	4874(5)	8582(4)	5874(4)
$C_{(20)}$	7912(4)	8492(3)	4019(3)	$C_{(47)}$	4105(5)	8085(5)	5833(4)
$C_{(21)}$	3849(4)	6516(3)	428(3)	$C_{(48)}$	4280(6)	7173(5)	5753(5)
$C_{(22)}$	4964(4)	7400(3)	988(3)	$C_{(49)}$	5256(7)	6779(5)	5258(5)
$C_{(23)}$	6051(4)	7492(3)	1751(3)	$C_{(50)}$	6063(5)	7284(4)	4804(4)
$C_{(24)}$	5726(4)	6577(3)	1901(3)				

In the allyl fragment of VIa, because of pronounced steric overloading, the molecule is "twisted" about the $C_{(18)}-C_{(19)}$ bond, and torsion angle $C_{(23)}C_{(18)}C_{(19)}C_{(20)}$ is 68.4(4)°. In this sort of rotation the absence of conjugation in the allyl fragment leads to virtual coincidence of the length of the $C_{(19)}=C_{(20)}$ bond [1.340(4) Å] with the standard value of the length of the $C_{(sp_2)}=C_{(sp_2)}$ bond (1.330 Å)[11], while the length of the $C_{(18)}-C_{(19)}$ single bond [1.510(6) Å] with the standard length of the $C_{(sp_2)}-C_{(sp_2)}$ bond [1.476(6) Å] [12].

Under the same conditions, from 2,6-di(p-methoxyphenyl)-4-phenylethynylpyrylium perchlorate (Ib) we were able to isolate and characterize dark-green monomethinecyanine Vb, in the PMR spectrum of which the resonance signal of the protons of the four methoxy groups is a singlet with a chemical shift of δ 3.53 ppm, which attests to the existence of conjugation between the pyran and pyrylium fragments in the Vb molecule and confirms that recyclization under the influence of O-nucleophiles to salt Ib does not occur (otherwise structure Vb would contain a p-methoxybenzoyl group rather than a benzoyl group in the allyl fragment).

On treatment with ammonia monomethinecyanine Vb is readily converted to 2,6-di(p-methoxyphenyl)-4-[1'-(2",6"-di(p-methoxyphenyl)-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl] pyridine (VIb). In the action of aniline on 2,6-diphenyl[di(p-methoxyphenyl)]-4-[1'-(2",6"-diphenyl[di(p-methoxyphenyl)]-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyrylium perchlorates (Va,b) the ring oxygen atom is replaced by nitrogen, and 1-phenyl-2,6-diphenyl[di(p-methoxyphenyl)]-4-[1'-(2",6"-diphenyl[di(p-methoxyphenyl)]-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyridinium perchlorates (VIIa,b) are formed.

Thus the high activity of the C≡C bond in ethynyl-substituted pyrylium salts, which was demonstrated in the case of their reactions with O-nucleophiles, makes further investigations of the properties of stable ethynyl carbonium ions promising.

EXPERIMENTAL

The IR spectra of thin layers of suspensions of the substances in mineral oil (NaCl prism) were recorded with a Specord IR-71 spectrometer. The PMR spectra of solutions in $CDCl_3$ were recorded with a Tesla BS-487 spectrometer (80 MHz) with hexamethyldisiloxane (HMDS) as the internal standard. The molecular mass was determined with an MS-30 mass spectrometer with an ionizing-emission energy of 70 eV.

The x-ray diffraction analysis of 2,6-diphenyl-4-[1'-(2",6"-diphenyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyridine (VIa) was carried out with crystals with the composition $C_{50}H_{35}NO_2$, which were grown from a mixture of isopropyl alcohol and acetonitrile and were triclinic: at 20°C a = 10.011(1), b = 15.012(1), c =15.067(1) Å, α = 117.239(4)°, β = 94.785(6)°, γ = 104.908(6)°, V = 1891.4(1) Å^3, Z = 2, space group P1.

The unit-cell parameters and the intensities of 4815 independent reflections were measured with a Hilger–Watts automatic four-circle diffractometer (λMo Kα, $\theta/2\theta$ scanning, $2° \leqslant \theta \leqslant 26°$). The structure was decoded by the direct method (with the MULTAN program) from 2763 reflections with $I \geqslant 2\sigma$ and was refined by the method of least squares within the block-diagonal anisotropic approximation from 2284 reflections with $(F) \geqslant 6\sigma$. The hydrogen atoms, the coordinates of which were calculated, were taken into account in refinement with fixed position and thermal (B_{iso} = 6 Å^2) parameters. The final convergence parameters were R = 0.043 and R_w = 0.038. All of the calculations were made with an Eclipse S δ 200 computer by means of the INEXTL program [13].

2,6-Diphenyl[di(p-methoxyphenyl)]-4-phenylethynylpyrylium perchlorates (Ia,b) were synthesized by the methods in [5, 6].

2,6-Di(p-methoxyphenyl)-4-[1'-(2",6"-di(p-methoxyphenyl)-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyrylium Perchlorate (Vb). A 0.98-g (2 mmole) sample of Ib was refluxed in 30 ml of ethanol for 2 h, after which the mixture was cooled, and the dark-green precipitate was removed by filtration to give 1.08 g (60%) of a product with mp 207-208°C (from isopropyl alcohol). IR spectrum: 1650 (C=O), 1600, 1580, 1510 (C=C), 1100 cm^{-1} (ClO_4^-). Found: C 71.1; H 5.1; Cl 4.4%. $C_{54}H_{43}ClO_{11}$. Calculated: C 71.8; H 4.8; Cl 3.9%.

2,6-Diphenyl-4-[1'-(2",6"-diphenyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyridine (VIa). A 0.86-g (2 mmole) sample of perchlorate Ia was refluxed for 0.5 h in 10 ml of ethanol, after which the mixture was diluted with 100 ml of ether, and the dark-violet precipitate was removed by filtration. Benzene (10 ml) was added to the precipitate, anbd a stream of dry ammonia was passed into the resulting suspension for 0.25 h. The benzene solution, which contained inorganic impurities, was filtered, the filtrate was evaporated, and the residue was chromatographed with a column packed with Al_2O_3 (1.5 by 40 cm) by elution with benzene. After removal of the solvent, the residue was recrystallized from isopropyl alcohol–acetonitrile (2:1) to give 0.29 g (59%) of a product with mp 217°C and R_f 0.15 (TLC, Al_2O_3, benzene). IR spectrum: 1660 (C=O), 1590, 1580 (C=C), 1210 cm^{-1} (C–O–C). Found: C 87.7; H 5.2; N 2.2%; M 681. $C_{50}H_{35}NO_2$. Calculated: C 88.1; H 5.1; N 2.0%.

2,6-Di(p-methoxyphenyl)-4-[1'-(2",6"-di(p-methoxypenyl)-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyridine (VIb). A stream of dry ammonia was passed into a suspension of 0.97 g (1 mmole) of perchlorate Vb in 20 ml of absolute benzene for 0.25 h, after which the benzene solution was filtered and evaporated, and the residue was chromatographed with a column (1.5 by 40 cm) packed with Al_2O_3 by elution with benzene. After removal of the solvent, the residue was recrystallized from isopropyl alcohol to give 0.55 g (69%) of a product with mp 140°C and R_f 0.13 (TLC, Al_2O_3, benzene). IR spectrum: 1653 (C=O), 1620, 1586 (C=C), 1246 cm^{-1} (C–O–C). PMR spectrum: 3.69 (12 H, broad s, four OCH_3), 6.15-7.88 ppm (31 H, m, 28 aromatic protons, two pyran protons, and one vinyl proton). Found: C 80.7; H 4.9; N 1.4%. $C_{54}H_{43}NO_6$. Calculated: C 80.9; H 5.3; N 1.7%.

1-Phenyl-2,6-diphenyl-4-[1'-(2",6"-diphenyl-4"-pyranylidene)-2'-phenyl-3'-benzoylallyl]pyridinium Perchlorate (VIIa). A 0.86-g (2 mmole) sample of perchlorate Ia was refluxed in 10 ml of ethanol for 0.5 h. The blue-violet precipitate that formed when the mixture was diluted with ether by a factor of 10 was removed by filtration and treated with 5 ml of aniline, and the mixture was allowed to stand for 20 h at 20°C. The addition of 50 ml of ether gave a dark-crimson precipitate. The yield of product with mp 202-203°C (from ethanol) was 1.22 g (72%). IR spectrum: 1650 (C=O), 1610, 1590 (C=C), 1260 (C–O–C), 1100 cm^{-1} (ClO_4^-). Found: C 77.9; H 4.8; Cl 3.9; N 1.1%. $C_{56}H_{40}ClNO_6$. Calculated: C 78.3; H 4.6; Cl 4.1; N 1.6%.

1-Phenyl-2,6-di(p-methoxyphenyl)-4-[1'-(2",6"-di-(p-methoxyphenyl-4")-pyranylidene-2'-phenyl-3'-benzoylallyl]pyridinium Perchlorate (VIIb). A 0.45-g (0.5 mmole) sample of perchlorate Vb was refluxed in 5 ml of aniline for 10 min, after which the mixture was diluted with ether by a factor of 10, and the violet precipitate was removed by filtration to give 0.44 g (91%) of a product with mp 185-186°C. IR spectrum: 1650 (C=O), 1607, 1560 (C=C), 1245 (C–O–C), 1100 cm^{-1} (Cl_4^-). Found: C 72.8; H 5.5; Cl 4.1; N 1.1%. $C_{60}H_{48}ClNO_{10}$. Calculated: C 73.6; H 4.9; Cl 3.6; N 1.4%.

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HETEROATOMIC DERIVATIVES OF AZIRIDINE.

15.* REACTION OF 1-(TRIETHYLSILYL)- AND 1-[2-(TRIALKYLSILYL)ETHYL]-AZIRIDINES WITH THIOLS

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UDC 547.717'245.07:543.422.4

The reaction of 1-(triethylsilyl)aziridine with alkanethiols proceeds with splitting out of aziridine and the formation of (alkylthio)triethylsilanes. The reaction of 1-(triethylsilyl)aziridine with 2-mercaptoethanol leads to 2-(triethylsilyloxy)ethanethiol; the same reaction in a closed system leads to [2-(2-aminoethylthiol)ethoxy]triethylsilane. 1-[2-(Trialkylsilyl)ethyl]aziridines react with 2-mercaptoethanol and with mercapto carboyxlic acids with opening of the aziridine ring.

Carbofunctional derivatives of organosilicon amines have a broad spectrum of biological activity. Their antiinflammatory, antispasmodic, and soporofic activity has been studied. These compounds are effective tranquilizers and agents for protection against radiation.

One of the methods for the synthesis of carbofunctional organosilicon amines is based on the reaction of (trialkylsilyl)- or (trialkoxysilyl) alkanethiols with aziridine, as well as on the reaction of 1-[(2-trialkylsilyl)ethyl]aziridines with thiols or thiophenols [3].

In order to obtain new types of biologically active organosilicon compounds, monomers for the synthesis of silicon-containing polymers, and complexones that are active with respect to transition metal ions we studied the reaction of 1-(triethylsilyl)aziridine (I) with alkanethiols and 2-mercaptoethanol and also accomplished the reaction of 1-[2-(trialkylsilyl)-ethyl]aziridines with 2-mercaptoethanol and mercaptosuccinic and 2-mercaptobenzoic acids.

Heating an equimolar mixture of 1-(triethylsilyl)aziridine (I) with propanethiol or butanethiol to 70°C with removal of the resulting aziridine by distillation leads to (alkylthio)triethylsilanes II and III in 60-65% yields. Thus cleavage of the Si—N bond rather than opening of the aziridine ring occurs in this case.

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*See [1] for Communication 14.

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR, Irkutsk 664033. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 891-893, July, 1988. Original article submitted December 1, 1986; revision submitted December 15, 1987.

0009-3122/88/2407-0730$12.50