THE ETHYNYL CARBOCATION.

4.* REACTION OF 4-PHENYLETHYNYLPYRYLIUM SALTS WITH C-NUCLEOPHILES

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The reaction of 4-phenylethynylpyrilium salts with indoles leads to indolylvinylpyrilium derivatives through attack of the β-carbon atom of the triple bond and subsequent intramolecular transfer of a proton from $C_{(3)}$ *of the indole ring to the sp-hybridized carbon atom of the allene group. The structure of 2,6-diphenyl-4-[2'-phenyl-2'-((β-methylindolyl)vinyl]pyrilium perchlorate was determined unequivocally by x-ray diffraction analysis and the most likely reaction scheme was indicated. The bond length distribution in the pyrilium cation indicates significant delocalization of positive charge.*

An important property of phenylethynylpyrilium salts is the addition of nucleophilic reagents in the side-chain of the pyrilium cation, leading to the formation of a functional group, while the ring is retained for further synthetic use [2, 3]. On the other hand the $C\equiv C$ bond activated by electron-withdrawing substituents, permits formation of new carbon—carbon bonds and generation of complex molecular structures such as norbornadienylpyrilium salts [1], which are difficult to obtain by other methods.

In previous work [2], we found that the products of the hydration of 4-phenylethynylpyrilium salts at the triple bond, namely, benzoylmethylenepyrans, undergo subsequent reaction with the starting salt as C-nucleophiles. The proposal that this process occurs through a cyclobutane transition state was based on literature analogies such as the conversion of indoles into benzazepine derivatives upon reaction with esters of acetylenecarboxylic acid [4, 5].

Thus, we studied the reactions of indole and N-methylindole with a series of 4-phenylethynylpyrilium salts in order to gain access to interesting hetaryl-substituted benzazepines.

In a series of experiments, the reaction of pyrilium salts (Ia)-(Ic) and indoles (IIa) and (IIb) gave highly colored products with proposed structure (IIIa)-(IIId) or (Va)-(Vd) (Scheme 1). The IR spectra of these products have bands at 1635-1605 and 1605-1510 cm^{-1}, characteristic for a $C=C$ double bond and pyrilium cation, and also strong bands at 1100 cm^{-1} (ClO_4^- anion). The PMR spectra of these compounds have one-proton singlets at δ 5.5 and 7.3 ppm, which may be assigned to vinyl protons. The existence of the pyrilium fragment in these products was indicated by the formation of the corresponding pyridine derivatives IVa and IVc or VIa and VIc upon their treatment with gaseous ammonia or ammonium acetate.

In a mass spectrometric study,† conjugation was found between the hetaryl fragments giving rise to maximal intensity for the molecular ion peak (M^+ 490) in the case of both possible structures IVc and VIc, although to a greater extent for VIc. (See scheme 1 on following page.)

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*For communication 3, see [1].

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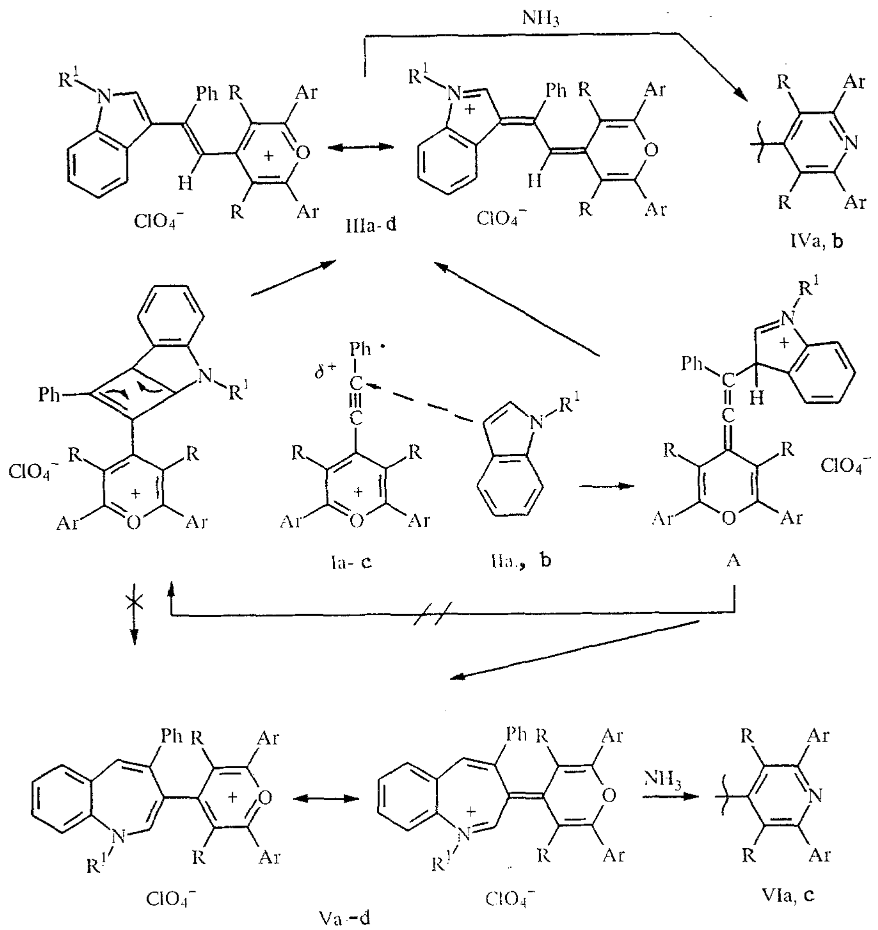
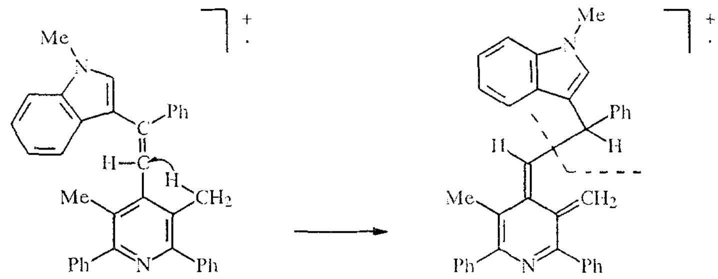
Scheme 1



III a Ar = Ph, R = H, R^1 = Me; b Ar = p-C_6H_4OMe, R = H, R^1 = Me; c Ar = Ph, R = Me, R^1 = Me;
d Ar = Ph, R = Me, R^1 = H

However, support for structure IVc is found in the peak with *m/z* 131, corresponding to an N-methylindole residue and the peaks with *m/z* 358 [(M — H) − N-methylindole)]$^+$ and 320 [(M − $C_{20}H_{16}N$)]$^+$ (*ortho* effect [6]):



The IR, PMR, and mass spectral data indicated that formation of indolylvinylpyrilium salts IIIa-IIId and not benzazepines Va-Vd is more probable in the reaction of 4-phenylethynylpyrilium perchlorates Ia-Ic with indoles. In order to find support for this conclusion and unequivocally determine the structure of the product of the reaction of Ia with IIa, we carried out the x-ray diffraction structural analysis of this product, which indicated that the structure corresponds to IIIa. Figure 1 shows a general view of the cation with bond lengths.

The mutual orientation of the two heterocyclic systems relative to the $C_{(9)}=C_{(10)}$ double bond indicates *trans* configuration of the cation (see Fig. 1). With the exception of phenyl ring C, which is oriented almost perpendicularly to the

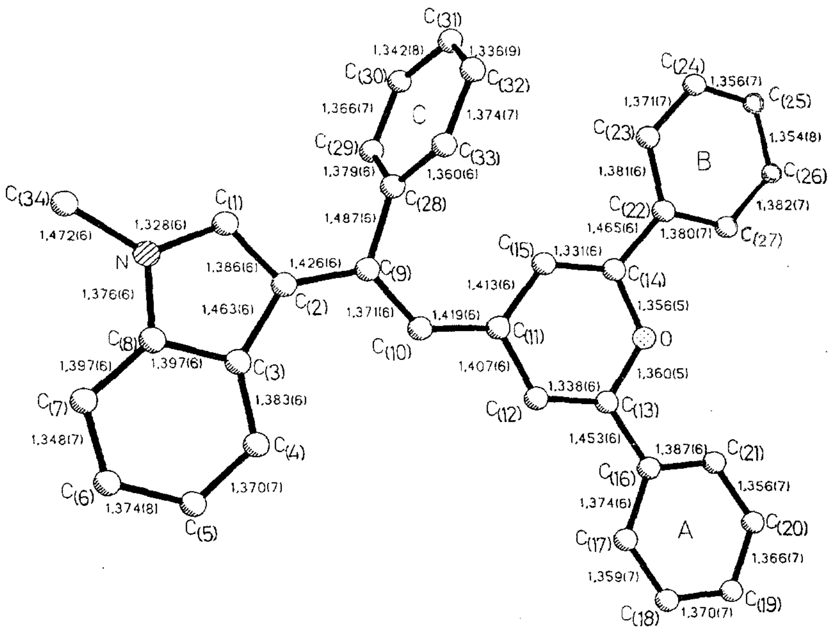


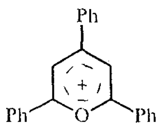
Fig. 1. General view of the cation with bond lengths.

plane P of the olefin chain $C_{(2)}—C_{(9)}=C_{(10)}—C_{(11)}$ (the C/P dihedral angle is 94.5°), the cation has a rather planar structure. Thus, the plane of the indole fragment makes an angle of 1.9° relative to the plane of the pyrilium ring, while this fragment makes an angle of 0.6° relative to plane P. Phenyl substituents A and B are twisted relative to the pyrilium ring by 7.4 and 6.9°, respectively. The $C_{(13)}—C_{(16)}$ (1.453(6) Å) and $C_{(14)}—C_{(22)}$ (1.465(6) Å) bond lengths are much shorter than the standard $C_{(aryl)}—C_{(aryl)}$ single bond length (1.487 Å [7]).

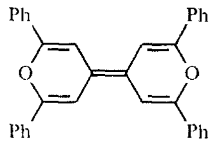
A tendency for equalization of the bond lengths is found in the $C_{(2)}—C_{(9)}=C_{(10)}—C_{(11)}$ chain. The $C_{(9)}=C_{(10)}$ formal double bond (1.371(6) Å) is significantly extended relative to the standard value for conjugated olefinic systems (1.331 Å) [7], while the $C_{(2)}—C_{(9)}$ (1.426(6) Å) and $C_{(10)}—C_{(11)}$ (1.419(6) Å) formal single bonds are much shorter than the standard value (1.455 Å). This finding indicates efficient π-electron delocalization in this fragment.

The observed significant distorted bond angles $C_{(2)}C_{(9)}C_{(10)}$ to 122.4(4)° and, especially, $C_{(9)}C_{(10)}C_{(11)}$ to 132.5(4)° are the result of steric strain due to the repulsion of the atoms of the pyrilium ring and phenyl substituent C, whose perpendicular orientation relative to the major body of the cation minimizes this repulsion. Nevertheless, two short nonbonding contacts remain in the cation: $C_{(15)}\cdots C_{(28)}$ (3.059(6) Å) and $C_{(15)}\cdots C_{(33)}$ (3.327(6) Å) (twice the van der Waals radius of the carbon atom is 3.40 Å [8]).

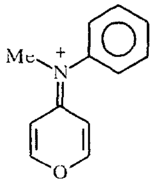
There have been only a few x-ray diffraction structural analyses of pyrilium salts. Structures have been determined for 2,4,6-triphenyl- [9-11], 2,4,6-trimethyl- and 2,6-di-*tert*-butyl- [12], and 2,6-dimethyl-4-chloromethylpyrilium salts [13]. In most of these studies, the precision of the structure determination was low and thus we selected the structure of only 2,4,6-triphenylpyrilium 1,1,3,3-tetracyanopropenide (VII) [9] as the most similar in structure and determination precision. On the other hand, it was of interest to compare the geometry of the charged pyrilium ring in the structure of IIIa and the central pyran ring in tetraphenyldipyranylidene (VIII) [14].



VII



VIII



IX

Comparison of the geometrical parameters of these rings in IIIa, VII, VIII, and IX (Table 1) indicates that some geometrical characteristics of this heterocycle in the structure of IIIa are very similar to the corresponding characteristics of the charged pyrilium heterocycle in VII (C—O, $C_{(11)}—C_{(12)}$, and $C_{(11)}—C_{(15)}$ bond lengths), while the $C_{(12)}—C_{(13)}$ and $C_{(14)}—C_{(15)}$ bond lengths in IIIa are virtually the same as the corresponding values in the pyran ring in VIII but differ by 0.03

TABLE 1. Major Geometrical Parameters of the Pyrilium or Pyran Heterocycles in IIIa and VII-IX

Compound	COC angle, deg	Mean bond length, Å		
		C—O	$C_{(12)}$—$C_{(13)}$ and $C_{(14)}$—$C_{(15)}$	$C_{(11)}$—$C_{(12)}$ and $C_{(11)}$—$C_{(15)}$
IIIa***	120,7	1,358	1,335	1,410
VII**	122,5	1,355	1,367	1,404
VIII*	118,2	1,389	1,337	1,444
IX***	119,6	1,357	1,343	1,419

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*Pyran ring; **Pyrilium ring; ***Resonance hybrid.

TABLE 2. Bond Angles ω (deg) in Cation IIIa

Angle	ω	Angle	ω	Angle	ω
$C_{(1)}NC_{(34)}$	125,7(4)	$C_{(2)}C_{(9)}C_{(10)}$	122,3(4)	$C_{(18)}C_{(19)}C_{(20)}$	118,7(5)
$C_{(8)}NC_{(34)}$	125,5(4)	$C_{(9)}C_{(10)}C_{(11)}$	132,6(4)	$C_{(19)}C_{(20)}C_{(21)}$	120,8(5)
$C_{(1)}NC_{(8)}$	108,8(4)	$C_{(10)}C_{(11)}C_{(15)}$	127,8(4)	$C_{(20)}C_{(21)}C_{(16)}$	121,3(4)
$NC_{(1)}C_{(2)}$	111,6(4)	$C_{(10)}C_{(11)}C_{(12)}$	118,8(4)	$C_{(14)}C_{(22)}C_{(23)}$	121,1(4)
$C_{(1)}C_{(2)}C_{(9)}$	123,4(4)	$C_{(15)}C_{(11)}C_{(12)}$	113,5(4)	$C_{(14)}C_{(22)}C_{(27)}$	121,2(4)
$C_{(3)}C_{(2)}C_{(9)}$	131,8(4)	$C_{(11)}C_{(12)}C_{(13)}$	123,5(4)	$C_{(27)}C_{(22)}C_{(23)}$	117,8(4)
$C_{(1)}C_{(2)}C_{(3)}$	104,8(4)	$C_{(12)}C_{(13)}C_{(16)}$	128,0(4)	$C_{(22)}C_{(23)}C_{(24)}$	120,3(4)
$C_{(2)}C_{(3)}C_{(8)}$	105,8(4)	$OC_{(13)}C_{(16)}$	112,8(4)	$C_{(23)}C_{(24)}C_{(25)}$	121,2(5)
$C_{(8)}C_{(3)}C_{(4)}$	117,8(4)	$C_{(12)}C_{(13)}O$	119,3(4)	$C_{(24)}C_{(25)}C_{(26)}$	119,6(5)
$C_{(2)}C_{(3)}C_{(4)}$	136,4(4)	$C_{(13)}OC_{(14)}$	120,7(3)	$C_{(25)}C_{(26)}C_{(27)}$	120,1(5)
$C_{(3)}C_{(4)}C_{(5)}$	119,4(4)	$OC_{(14)}C_{(22)}$	112,1(4)	$C_{(26)}C_{(27)}C_{(22)}$	121,0(5)
$C_{(4)}C_{(5)}C_{(6)}$	121,4(5)	$C_{(22)}C_{(14)}C_{(15)}$	128,1(4)	$C_{(9)}C_{(28)}C_{(29)}$	120,8(4)
$C_{(5)}C_{(6)}C_{(7)}$	122,1(5)	$OC_{(14)}C_{(15)}$	119,9(4)	$C_{(9)}C_{(28)}C_{(33)}$	121,3(4)
$C_{(6)}C_{(7)}C_{(8)}$	116,8(5)	$C_{(14)}C_{(15)}C_{(11)}$	123,1(4)	$C_{(33)}C_{(28)}C_{(29)}$	117,7(4)
$C_{(7)}C_{(8)}C_{(3)}$	122,7(4)	$C_{(13)}C_{(16)}C_{(17)}$	121,1(4)	$C_{(28)}C_{(29)}C_{(30)}$	120,0(4)
$C_{(7)}C_{(8)}N$	128,3(4)	$C_{(13)}C_{(16)}C_{(21)}$	121,8(4)	$C_{(29)}C_{(30)}C_{(31)}$	120,8(5)
$C_{(3)}C_{(8)}N$	109,0(4)	$C_{(21)}C_{(16)}C_{(17)}$	117,1(4)	$C_{(30)}C_{(31)}C_{(32)}$	120,3(5)
$C_{(2)}C_{(9)}C_{(28)}$	117,8(4)	$C_{(16)}C_{(17)}C_{(18)}$	121,6(5)	$C_{(31)}C_{(32)}C_{(33)}$	119,7(5)
$C_{(28)}C_{(9)}C_{(10)}$	119,9(4)	$C_{(17)}C_{(18)}C_{(19)}$	120,6(5)	$C_{(32)}C_{(33)}C_{(28)}$	121,3(5)

Å from the corresponding values in salt VII. The COC bond angle in IIIa (120.7(3)°) is intermediate between 122.5° in the cation of salt VII and 118.2° in VIII. In all these pyrilium cations, this angle significantly exceeds 120° and ranges from 121.9° [13] to 126° [10] (Table 2).

The quantum-chemical calculation carried out by Tamamura et al. [9] showed that the positive charge in the cation of salt VII is concentrated mainly on the oxygen atom and adjacent carbon atoms in the heterocycle. The lack of accord of some of the geometrical parameters for the pyrilium rings in IIIa and VII may be attributed to different distribution of positive charge or, more precisely, the more efficient distribution of positive charge in the case of IIIa. This hypothesis was supported by the similarity of the geometry of the heterocycle examined in salt IIIa and in 2,6-dimethyl-4-(*p*-nitrophenyl)iminopyran methobromide (IX) [15] (Table 3). Sammes et al. [15] carried out an interesting study of variation in the geometry of the iminopyran fragment upon going from neutral 2,6-dimethyl-4-(*p*-nitrophenyl)iminopyran through its hydrobromide to methobromide IX. While the positive charge in hydrobromide is localized mainly on imine nitrogen atom, it is delocalized in cation IX to the heterocycle and the cation in IX is a resonance hybrid with a significant contribution of the pyrilium form.

The bond lengths in the indole system in cation IIIa should be compared with the mean values found for 40 indole structures tabulated by Allen et al. [7]. Significant shortening of the N—$C_{(1)}$ bond to 1.328(6) Å was found in the five-membered heterocycle of the indole system in IIIa in comparison to the corresponding mean value for indoles (1.370 Å) and extension of the $C_{(1)}$—$C_{(2)}$ bond to 1.386(6) Å (vs. 1.364 Å) and of the $C_{(2)}$—$C_{(3)}$ bond to 1.463(6) Å (vs. 1.434 Å). Such change in the bond lengths in the indole system of cation IIIa indicates a redistribution of the π electrons and partial delocalization of positive charge to its nitrogen atom.

In reviewing the structural features of the cation of IIIa, namely, a planar, conjugated main fragment, geometrical amphoterism of the O-heterocycle, and an unusual bond length distribution in the N-heterocycle, we may conclude that there

TABLE 3. Atomic Coordinates ($\times 10^4$, $\times 10^3$... for the H Atoms) and Temperature Factors (B_{iso}^{eq} for the nonhydrogen atoms and B_{iso} for the hydrogen atoms) in the Structure of IIIa

Atom	x	y	z	B, A^2	Atom	x	y	z	B, A^2
$Cl_{(1)}$*	0	1/2	0	10,1(1)	$C_{(12)}$	3943(4)	4601(4)	1803(4)	4,5(2)
$Cl_{(2)}$*	4492(3)	9707(3)	4786(3)	7,2(2)	$C_{(13)}$	3801(4)	3816(4)	2468(3)	3,9(1)
$O_{(1)}$*	1363(7)	4782(6)	-126(8)	9,3(4)	$C_{(14)}$	5973(4)	4822(3)	3551(3)	3,8(1)
$O_{(2)}$*	635(10)	6462(8)	176(10)	12,1(5)	$C_{(15)}$	6118(5)	5597(4)	2862(4)	4,7(2)
$O_{(3)}$*	-316(11)	4905(8)	992(8)	11,6(4)	$C_{(16)}$	2645(4)	2812(3)	2400(3)	3,8(1)
$O_{(4)}$*	835(10)	5191(10)	788(9)	14,1(5)	$C_{(17)}$	1436(5)	2633(4)	1661(4)	5,2(2)
$O_{(5)}$*	4502(10)	10925(9)	4875(8)	11,2(4)	$C_{(18)}$	325(5)	1723(4)	1623(5)	6,4(2)
$O_{(6)}$*	4135(10)	9219(8)	3705(7)	10,3(4)	$C_{(19)}$	384(5)	948(4)	2323(5)	6,2(2)
$O_{(7)}$*	3301(10)	9464(9)	5321(7)	10,8(4)	$C_{(20)}$	1582(5)	1107(4)	3057(4)	5,2(2)
$O_{(8)}$*	4994(13)	9300(9)	5307(9)	13,7(5)	$C_{(21)}$	2689(5)	2016(4)	3099(4)	4,7(2)
O	4817(3)	3931(2)	3340(2)	3,9(1)	$C_{(22)}$	6931(4)	4790(4)	4510(3)	3,8(1)
N	6389(4)	9467(3)	-644(3)	4,6(1)	$C_{(23)}$	8087(5)	5688(4)	4917(4)	4,9(2)
$C_{(1)}$	6817(5)	9020(4)	213(4)	4,6(2)	$C_{(24)}$	8968(5)	5648(4)	5839(4)	5,9(2)
$C_{(2)}$	5888(4)	7999(4)	287(3)	3,7(1)	$C_{(25)}$	8737(6)	4730(5)	6367(4)	6,2(2)
$C_{(3)}$	4763(5)	7829(4)	2638(4)	4,0(2)	$C_{(26)}$	7606(6)	3841(5)	5988(4)	6,7(2)
$C_{(4)}$	3521(5)	7017(4)	-1056(4)	5,0(2)	$C_{(27)}$	6705(5)	3866(4)	5061(4)	6,0(2)
$C_{(5)}$	2713(5)	7154(4)	-1977(4)	5,8(2)	$C_{(28)}$	7362(4)	7779(3)	1974(3)	3,7(1)
$C_{(6)}$	3121(6)	8079(5)	-2498(4)	6,4(2)	$C_{(29)}$	8623(5)	7498(4)	1809(4)	4,9(2)
$C_{(7)}$	4313(5)	8900(4)	-2124(4)	5,2(2)	$C_{(30)}$	9759(5)	7829(4)	2619(5)	6,7(2)
$C_{(8)}$	5137(5)	8761(4)	-1185(4)	4,2(2)	$C_{(31)}$	9656(6)	8401(4)	3591(5)	7,5(2)
$C_{(9)}$	6080(4)	7345(4)	1138(3)	3,8(1)	$C_{(32)}$	8464(7)	8720(4)	3758(4)	7,0(2)
$C_{(10)}$	5136(5)	6345(4)	1202(4)	5,1(2)	$C_{(33)}$	7309(5)	8397(4)	2954(4)	5,2(2)
$C_{(11)}$	5100(4)	5557(4)	1952(4)	4,2(2)	$C_{(34)}$	7113(6)	10554(4)	-950(4)	6,4(2)
$H_{(1)}$	760(3)	934(2)	615(2)	2,7(7)	$H_{(23)}$	827(4)	632(3)	461(3)	5,5(9)
$H_{(4)}$	323(3)	639(2)	-78(2)	3,1(7)	$H_{(24)}$	961(3)	620(3)	604(3)	3,9(8)
$H_{(5)}$	201(3)	660(3)	-228(3)	4,3(8)	$H_{(25)}$	927(4)	478(3)	700(3)	5,1(9)
$H_{(6)}$	269(3)	815(3)	-303(3)	3,8(8)	$H_{(26)}$	733(4)	326(3)	626(3)	7,7(11)
$H_{(7)}$	463(3)	948(2)	-241(30)	3,7(8)	$H_{(27)}$	609(3)	330(3)	483(3)	4,3(8)
$H_{(10)}$	448(3)	613(3)	75(3)	4,0(8)	$H_{(29)}$	864(3)	710(3)	118(3)	3,2(7)
$H_{(12)}$	332(3)	450(2)	124(2)	2,0(6)	$H_{(30)}$	1043(3)	765(3)	246(3)	4,4(8)
$H_{(15)}$	678(3)	605(2)	300(2)	1,5(6)	$H_{(31)}$	1037(4)	852(3)	409(3)	6,4(10)
$H_{(17)}$	139(3)	304(2)	128(2)	2,0(7)	$H_{(32)}$	833(4)	910(3)	433(3)	6,0(10)
$H_{(18)}$	-35(3)	161(3)	121(3)	4,1(8)	$H_{(33)}$	662(3)	861(2)	305(2)	2,3(7)
$H_{(19)}$	-30(3)	34(3)	233(3)	4,0(8)	$H_{(34A)}$	795(5)	1082(4)	-69(4)	9,5(13)
$H_{(20)}$	163(4)	55(3)	351(3)	5,9(10)	$H_{(34B)}$	662(6)	1109(5)	-76(5)	15,9(17)
$H_{(21)}$	340(3)	214(2)	349(2)	2,1(7)	$H_{(34C)}$	720(4)	1044(3)	-152(3)	5,3(9)

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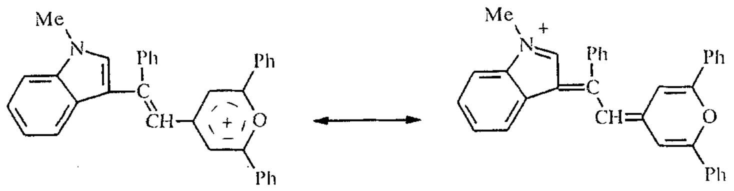
*The ClO_4^- anions are randomly disordered. The $Cl_{(2)}$ atoms and all the oxygen atoms occupy two positions with 0.5 occupancy.

is considerable delocalization of the positive charge in this cation. The observed structure of the cation may be described by the participation of two limiting resonance forms:



The observed geometry of the ClO_4^- anions is highly distorted due to their disorder and does not merit discussion. For the same reason, we should not examine the contacts between the anions and cations. On the other hand, the observed contacts between the cations (the shortest of which are $C_{(3)}\cdots C_{(13')}$ (3.455(6) Å) and $C_{(5)}\cdots C_{(14')}$ (3.448(7) Å) between cations related by a symmetry center) and the absence of overlapping of the cations in the crystalline structure of IIIa indicate low probability for the existence of interactions other than van der Waals and electrostatic forces such as stacking interactions in the crystal of salt IIIa.

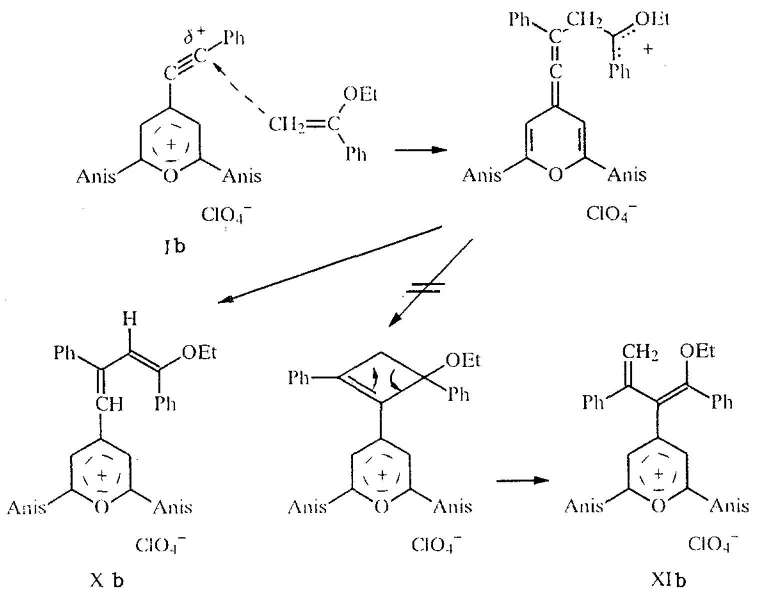
Thus, the x-ray diffraction structural analysis data permit an unequivocal selection of the structure of product IIIa and suggest the most likely reaction scheme.

The reaction of 4-phenylethynylpyrilium salts proceeds through a pathway different from that for benzylmethylenepyran [2]. Otherwise, benzazepines Va-Vd would have been formed. The formation of indolylvinylpyrilium salts IIIa-IIId may be attributed to a stepwise mechanism for reaction of the partners, while the allene intermediates generated A may display dual behavior: the *sp*-hybridized carbon atom may attack either $C_{(2)}$ of the indole as a nucleophile or the hydrogen atom at $C_{(3)}$ of the indole system as a base.

The second pathway is probably most favorable since the two heterocyclic fragments are immediately aromatized with the formation of a conjugated system with the greatest possible delocalization of the positive charge. Such delocalization is also facilitated by steric factors. Plieninger and Wild [4] have described such intramolecular deprotonation. The lack of such an interaction in the reactions of ethynylpyrilium salts with benzylmethylenepyrans [2] may occur since the required approximation of the *sp*-hybridized atom in one fragment of the intermediate adduct with the electrophilic site in another such adduct required for formation of the cyclobutene transition state is provided in the latter case by the sterically favorable π—σ donor—acceptor interaction of the pyrilium and pyran rings, which may closely approach one another. Such complementation is not achieved in reactions with indole and the pathway involving intramolecular proton transfer becomes predominant.

Support for this proposal is found in the reaction of 2,6-di-(*p*-methoxyphenyl)-4-phenylethynylpyrilium perchlorate Ib with ethoxystyrene, which behaves similarly to indole. This is unequivocally indicated by the PMR spectrum of the final product Xb, which shows one-proton singlets at δ 6.137 and 5.73 ppm with the absence of signals for the methylene group protons of product XIb (Scheme 2).

Scheme 2



EXPERIMENTAL

The IR spectra of suspensions in vaseline oil were taken on a Specord IR-75 spectrophotometer using NaCl plates. The PMR spectra were taken on a Tesla BS-487 spectrometer at 80 MHz with HMDS as the internal standard. The mass spectral data were obtained on a Varian MAT-113 GC/MS at 70 eV.

TABLE 4. Indices of Indolylvinylpyrilium Perchlorates IIIa-IIId

Compound	Chemical formula	mp, °C	Time, h	IR spectrum, cm^{-1}	PMR spectrum, δ, ppm, solvent	Yield, %
IIIa	$C_{34}H_{26}ClNO_5$	310	2	1634, 1587, 1547, 1100	3,93 (3H, s, CH_3); 7,3...8,0 (23H, m, 1H CH, 22H Ar); DMF	81
IIIb	$C_{36}H_{30}ClNO_7$	257	1	1635, 1604, 1552, 1260, 1100	3,52 (6H, s, 2 OCH_3); 4,05 (3H, s, CH_3); 6,62...7,75 (21H, m, 1H CH, 20 H Ar); CF_3COOH	78
IIIc	$C_{36}H_{30}ClNO_5$	168	1	1610, 1545, 1512, 1100	2,0 (6H, s, 2 CH_3); 3,67 (3H, s, CH_3); 7,05...7,6 (21H, m, 1H CH, 20 H Ar); $CDCl_3$	85
IIId	$C_{35}H_{28}ClNO_5$	165	1	3225, 1614, 1587, 1540, 1100	2,02 (6H, s, 2CH_3); 6,63 (1H, s, CH); 7,25...7,62 (20H, m, Ar); 10,0 (1H, s, NH); $CDCl_3$	84

The red, triclinic crystals of 2,6-diphenyl-4-[2′-phenyl-2′-(β-methoxyindolyl)vinyl]pyrilium perchlorate (IIIa) with a green hue have the following unit cell parameters: a = 9.7762(9); b = 12.1620(10), c = 12.4550(10) Å, α = 97.423(8), β = 96.246(7), γ = 102.862(8)°, V = 1417.1(2) $Å^3$, z = $2[C_{34}H_{26}NO]^+[ClO_4]^-$, d_{calc} = 1.322 g/cm^3, space group $P\bar{1}$.

The unit cell parameters and intensities of 2650 reflections were measured on a Hilger-Watts four-circle automatic diffractometer using λMoK_α radiation, graphite monochromator, and θ/2θ scanning up to θ < 30°. The structure was solved by the direct method using the MULTAN program and refined by the method of least squares, initially in the isotropic approximation and then in the anisotropic block-diagonal approximation. The unit cell contains two crystallographically independent ClO_4^- anions. The chlorine atom of one of these anions is located at a center of inversion (0, ½, 0), while the chlorine atom of the other is located near a center of inversion (½, 0, ½). Thus, the two anions are disordered, which is rather common for perchlorate anions, including those found at general positions. All the hydrogen atoms were located in the difference maps and were included in the refinement in the isotropic approximation. The final R = 0.053 (R_W = 0.063) using 2149 reflections with $F^2 \geq 3\sigma$. All the calculations were carried out on an Eclipse S/200 computer using the INEXTL programs [16]. The atomic coordinates are given in Table 3.

The characteristics of IIIa-IIId are given in Table 4.

The elemental analysis data for C, H, Cl, and N for IIIa-IIId, IVa, IVc, and Xb corresponded to the calculated values.

Perchlorates Ia-Ic were prepared according to reported procedures [17-19].

2,6-Diaryl-3,5-di-R-4-[2′-phenyl-2′-(β-R^1-indolyl)vinyl]pyrilium Perchlorates IIIa-IIId. A solution of 5 mmoles of the corresponding indole in 5 ml absolute acetonitrile was added dropwise with ice cooling to a stirred suspension of 5 mmoles 4-phenylethynylpyrilium salt Ia-Ic in 15 ml absolute acetonitrile and stirred at reflux (see Table 4). After cooling, the indolylvinylpyrilium salt precipitate was filtered off. An additional portion of the product was precipitated from the mother liquor by the addition of ether.

2,6-Diphenyl-4-[2′-phenyl-2′-(β-N-methylindolyl)vinylpyridine IVa ($C_{34}H_{26}N_2$). A stream of ammonia was passed through a suspension of 0.56 g (1 mmole) perchlorate IIIa in a mixture of 10 ml benzene and 2 ml acetonitrile for 20-30 min until the precipitate dissolved. The solvent was evaporated off and the residue was eluted from a 1.5×40-cm alumina column with benzene. The solvent was removed and the precipitate was recrystallized from 2-propanol, mp 139-140°C, R_f 0.8. IR spectrum: 1593, 1580, 1525 cm^{-1}. PMR spectrum in $CDCl_3$: 3.52 (3H, s, CH_3), 6.67 (1H, s, CH), 7.07-7.95 ppm (22H, m, Ar). The yield of IVa was 0.25 g (54%).

1,6-Diphenyl-3,5-dimethyl-4-[2′-phenyl-2′-(β-N-methylindolyl)vinyl]pyridine IVc ($C_{36}H_{30}N_2$). A mixture of 0.59 g (1 mmole) perchlorate IIIc and 10 g ammonium acetate was heated at reflux in 20 ml acetic acid for 1 h and, then, diluted with 100 ml water. The mixture was extracted with benzene. The benzene extracts were washed with water until the wash water was at pH 7 and evaporated. The residue was recrystallized from 1:1 2-propanol—acetonitrile, mp 207°C. IR spectrum: 1606, 1594, 1520 cm^{-1}. PMR spectrum in $CDCl_3$: 2.05 (6H, s, $2CH_3$), 3.57 (3H, s, CH_3), 6.52-7.45 ppm (21H, m, 1H CH, 20H Ar). The yield of IVc was 0.28 g (57%).

After removal of the pyridine with mp 207°C from the mother liquor, a product with mp 196°C was obtained on the following day, which was a mixture of *E* and *Z* isomers. IR spectrum: 1614, 1605, 1567, 1547, 1533 cm^{-1}. PMR spectrum in $CDCl_3$: 2.02 (6H, s, $2CH_3$), 2.07 (6H, s, $2CH_3$), 3.51 (2H, s, CH_3), 3.58 (3H, s, CH_3), 6.5-7.7 ppm (21H, m, 1H CH, 20H Ar).

2,6-Di-(*p*-methoxyphenyl)-4-(2′,4′-diphenyl-4′-ethoxy-1′,3′-butadienyl)pyrilium Perchlorate Xb ($C_{37}H_{33}ClO_8$). A sample of 0.7 ml (3.8 mmoles) α-ethoxystyrene was added to a solution of 1.47 g (3 mmoles) perchlorate Ib in 50 ml absolute acetonitrile and heated at reflux for 5 h. Ether was added and the mixture was filtered to give 1.11 g (58%) yellow-orange precipitate with mp 252°C (from CH_3CN). IR spectrum: 1620, 1594, 1540, 1267, 1233, 1100 cm^{-1}. PMR spectrum in CF_3CO_2H: 0.97 (3H, t, CH_2CH_3), 3.48 (6H, s, $2OCH_3$), 4.0 (2H, q, CH_2CH_3), 5.73 (1H, s, CH=C), 6.137 (1H, s, CH=C), 6.38-7.58 ppm (20H, m, Ar).

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