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Spectroscopic Study of Reaction of Propargyl Bromide with Pyridine

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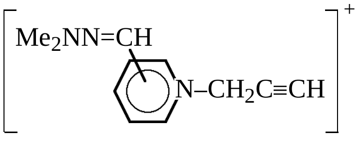
Abstract—Pyridine was reacted with propargyl bromide to obtain the dibromide $[C_5H_5NCH{=}CHCH{=}CHCH{=}CHC_5H_5N]^{2+}$ $2Br^-$. The effect of the vinyl group on its UV spectrum is qualitatively interpreted using the results of nonempirical quantum-chemical calculations (basis HF/6-31G*).

It is known [1] that *N*,*N*-dimethylhydrazones react with methyl iodide in anhydrous ethanol to give *N*,*N*,*N*-trimethylhydrazonium iodides $Me_3N^+{-}N{=}CRR'$ I^- (R = R' = Ph, $PhCH_2$, *i*-Bu; R = Me, R' = Ph; R = Me, R' = $PhCH_2$).

We earlier found [2] that reactions of *N*,*N*-dimethylhydrazones with propargyl bromide and 1,3-dibromopropyne (in diethyl ether, methanol, or acetonitrile at 20°C) involve alkylation by the tertiary nitrogen atom and yields bromides $RCH{=}NN^+(Me)_2(CH_2C{\equiv}CR')$ Br^- (R = Me, Ph, 2-thienyl; R' = N, Br).

With 4(3)-formylpyridine hydrazones, however, the reaction pathways changes considerably. This is primarily evidenced by the appearance of an intense color and the lack of ν(C≡C) and ν(≡C–H) bands in the IR spectrum of one of the isolated reaction products. These data led us to propose that the heterocyclic fragment competes with amine in the reactions in question, and at their initial stages propargyl bromide adds to the pyridine nitrogen atom to give a cation.



To verify this hypothesis, we studied reaction of pyridine with propargyl bromide. It was found that the reaction time and the structure of the reaction products are strongly dependent on the reactant ratio and the medium.

The IR spectrum of the reaction product formed with excess $BrCH_2C{\equiv}CH$ in the reaction mixture slightly differs from the spectrum of *N*-ethylpyridinium cation in the 1700–400 cm^{-1} range. Note that the most characteristic feature of the IR spectrum of $[C_5H_5NCH_2CH_3]^+$ Br^- (**I**) is the high-frequency shift of the strong stretching vibration bands of the pyridinium ring from 1430, 1530, and 1600 cm^{-1} (pyridine) to 1480 and 1620 cm^{-1}. The ν(C–H) band of the CH_2N group of this cation is located in a region characteristic of salts and has a maximum at ~3010 cm^{-1}. The bending vibration bands of the five adjacent hydrogen atoms of the heteroring, located in the spectrum of pyridine at 700 and 740 cm^{-1}, are shifted in the spectrum of the cation to 680 and 780 cm^{-1}. Along with these bands, the high-frequency region of the IR spectrum of the reaction product shows ν(C≡C) (2110 cm^{-1}) and ν(≡C–H) (3120 cm^{-1}) bands. Thus, the IR spectrum provides unambiguous evidence showing that the reaction product formed with excess is the salt $[C_5H_5NCH_2C{\equiv}CH]^+$ Br^- (**II**).

Since the unsaturated fragments of the cation $[C_5H_5NCH_2C{\equiv}CH]^+$ are intervened by a methylene unit, we might expect that the UV spectrum of a solution of salt **II** would be similar to the spectra of solutions of salts of *N*-alkylpyridinium cations. The UV spectrum of the *N*-ethylpyridinium cation, we obtained in the present work, is identical to those reported in the literature [3–5] and contains a fine-structured band at 35 000–41 000 cm^{-1}. The salt of this cation is readily soluble in aprotic solvents, and its absorption maximum, for instance, in acetonitrile is at 38 600 cm^{-1}. The vibronic splitting here is ~600 cm^{-1} (Fig. 1). We found that the spectra of the two cations in polar media are not only similar, but also fully identical to each other, both in shape and in position (Figs. 1a and 1b). The spectrum in the low-polarity $CHCl_3$ contains, along with the band of the ion pair, a $Br^- \rightarrow$ cation charge-transfer band (Fig. 1c). Such band is also characteristic of pyridinium salts [6].

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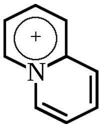
The reaction of propargyl bromide with excess pyridine gave a complex intractable mixture of products. Therefore, its composition was studied by spectral methods.

The IR spectrum of the product formed with excess pyridine or with equimolar reactant ratio characteristically lacks C≡C and ≡C–H absorption bands but shows enhanced absorption in the region of stretching vibrations of the pyridinium C=C and C=N bonds (1630 cm^{-1}).

By measuring the IR spectra at certain intervals under conditions when the reaction is sufficiently slow, i.e. at equimolar reactant ratio in acetonitrile, we could trace the overall reaction dynamics. It proved that the initial stage involves formation of a new cation, a precursor of the final reaction product. One might suggest that it is an *N*-allylpyridinium cation incorporated as a structural unit in the final reaction product. This suggestion follows from a comparison of the IR spectrum of the final reaction product with the spectrum of *N*-allylpyridinium bromide obtained from pyridine and allyl bromide (Figs. 2a and 2b). However, this hypothesis conflicts with the intense color of the final product, in view of the fact that the *N*-allylpyridinium cation has no visible absorption bands. Therefore, in further studies we used UV spectroscopy.

According to UV data, if the propargyl bromide : pyridine ratio is slightly lower than 2 : 1, one more salt is accumulated in the reaction mixture. The absorptiom maximum of the cation of this salt is strongly shifted (by ~8500 cm^{-1}) to low frequencies compared with those of *N*-alkylpyridinium cations (Fig. 3a). The absorption band of the new species, unlike that of *N*-alkylpyridinium cations, is modulated by the vibration frequency 1000–1200, rather than 600 cm^{-1}, and has the strongest 0→0 component. This vibration range is characteristic of an exocyclic double bond weakened in the electronically excited state. In its position (ν_{max} ~30 000 cm^{-1}) and fine structure the new band is close to the absorption bands of heterocyclic cations like **A** having two double bonds at the pyridinium nitrogen atom (Table 1).



A

Importantly, the counterion–couterion charge-transfer band here is shifted as strongly as the intrinsic absorption band of the cation. The charge-transfer band is already in the visible spectral range (23 400 cm^{-1}), thus imparting color to the sample, and is registered even in such a polar solvent as acetonitrile. This fact points to an unusually high resistance of the ion pair to dissociation into free ions.

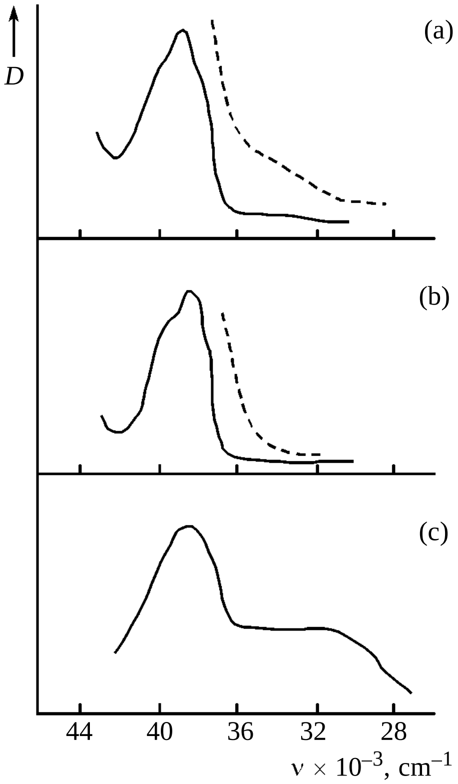


Fig. 1. UV spectra of (a) $[C_5H_5NCH_2CH_3]^+$ in MeCN, (b) $[C_5H_5NCH_2C{\equiv}CH]^+$ in MeCN, and (c) ion pair $[C_5H_5NCH_2C{\equiv}CH]^+ Br^-$ in $CHCl_3$. (Dashed lines) Bands recorded for highly concentrated solutions.

At equimolar reactant ratio, a compound is formed, whose UV spectrum exhibits a well-defined third band with fine structure. This band is similar in shape to that of the pyridinium cation, but its ν_{max} is 27 500 cm^{-1} (Fig. 3b). The charge-transfer band overlaps with a weak band of different nature, presumably belonging to some structurally more complex cation. Evidence for this assignment comes from the fact that the latter band is present in the spectrum of aqueous silutions (Fig. 3c) of the reaction product obtained with excess pyridine. The spectra all contain an *N*-alkylpyridinium absorption band. Consequently, this fragment enters into the composition of the reaction products. Inspection of data in Table 1 shows that the effect of the pyridine nitrogen atom on the absorption maximum of the cation is roughly additive (on average, $\Delta\nu_{max}$ is 3800 cm^{-1}). This value is smaller by only 700 cm^{-1} than the increment of a double bond elongating the conjugation chain in homoannular

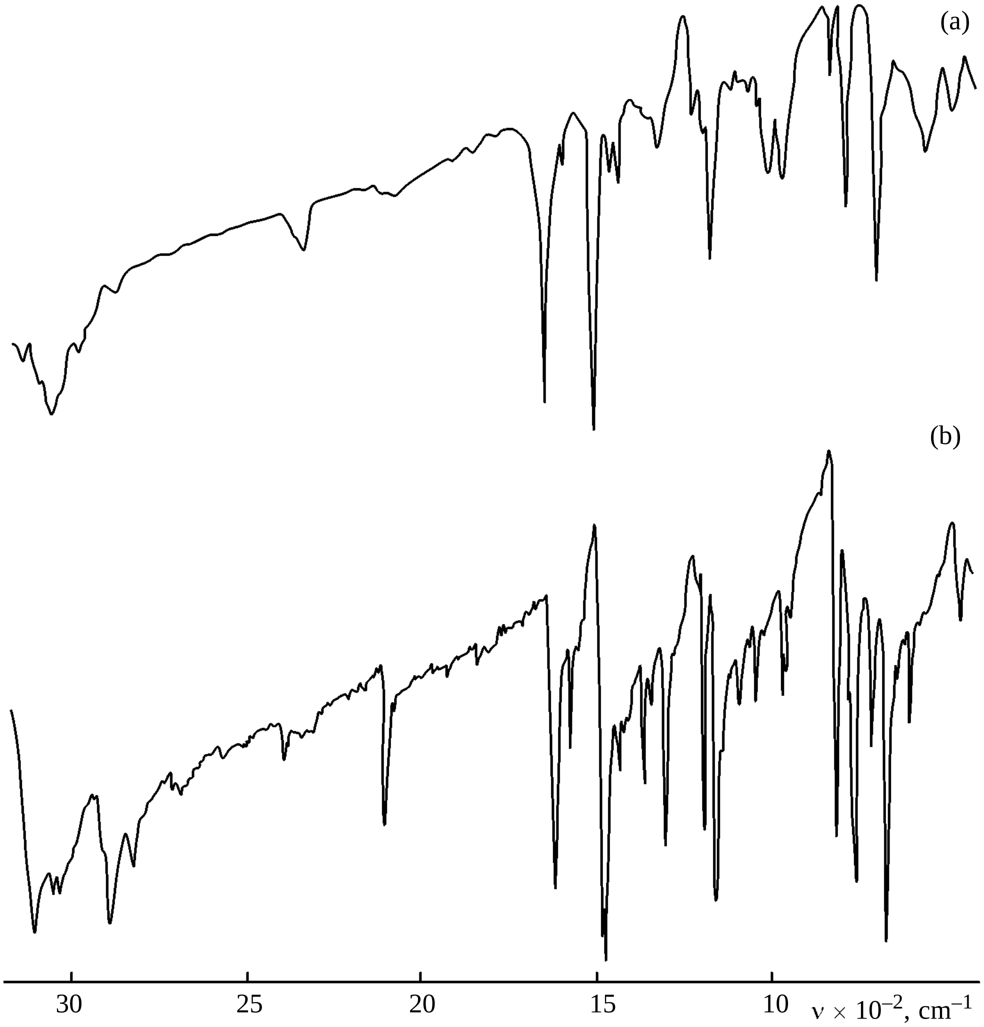


Fig. 2. IR spectra of (a) $[C_5H_5NCH_2CH=CH_2]^+Br^-$ and (b) the final reaction product of pyridine with $BrCH_2C{\equiv}CH$.

dienes (4500 cm^{-1}) [10]. As known, increasing number of double bonds diminish the red shift of the absorption band of a polyene. For instance, in the $H(CH=CH)_nH$ series, in going from $n = 3$ to $n = 4$, $\Delta\nu_{max}$ is 4400 cm^{-1} and gets smaller for further pairs: 3000 (n = 4–5), 2400 (n = 5–6) and 1900 (n = 6–7) cm^{-1} [10].

The smallest shift of the UV spectrum with respect to that of the *N*-ethylpyridinium cation [8400 cm^{-1} (Table 1)] is characteristic of a cation in which the pyridine nitrogen atom is attached to a polyene chain containing no more than three C=C bonds. The same analysis is readily performed for the other cations observed in the UV spectrum.

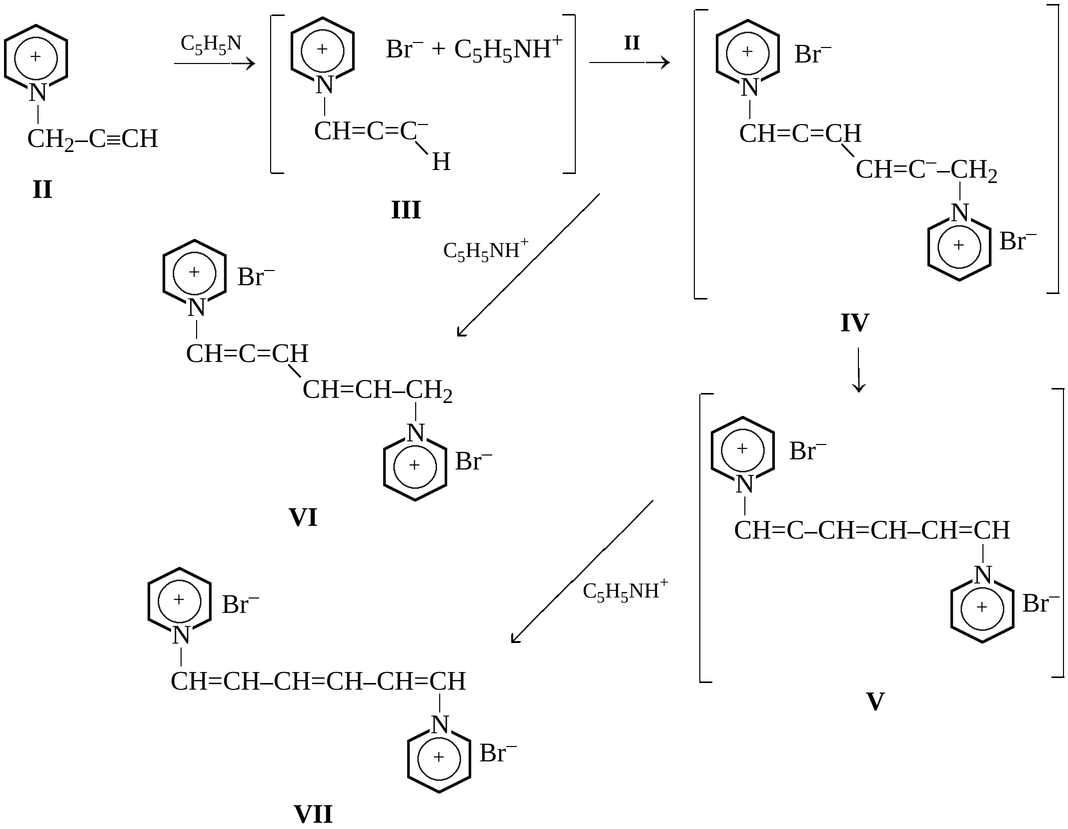
Thus, the initial stage of cation formation with excess pyridine can be represented by Scheme 1.

The ^{13}C NMR spectrum of the reaction products of pyridine with propargyl bromide is given in Fig. 4. As seen, we deal with a complex mixture of structurally similar compounds, and, therefore, traditional ^{13}C, not to mention ^1H NMR spectroscopies are fully unsuitable here.

This mixture of products was examined in terms of quantitative approaches of NMR spectroscopy of multicomponent organic mixtures, as well as using multipulse experiments to obtain the subspectra of primary and tertiary and secondary and quaternary carbon atoms [11].

The lack in the ^{13}C NMR spectrum (Fig. 4, Table 2) of C≡C carbon signals suggests complete conversion of propargyl bromide. Calculations showed that the carbon atoms giving signals at δ_C 118–150 ppm comprise 89% of the total number of

Scheme 1.



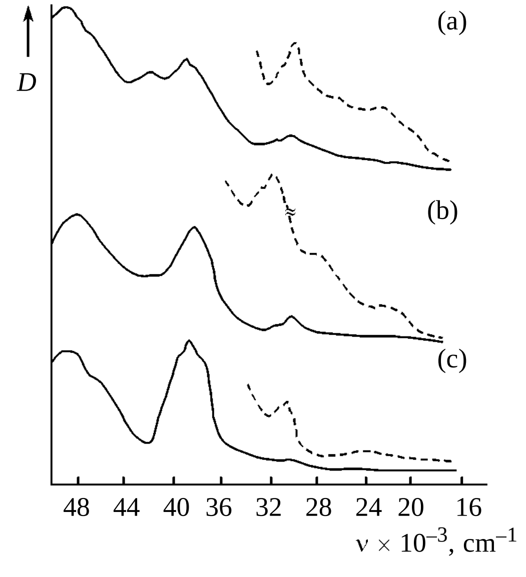


Fig. 3. UV spectra of the reaction products of pyridine with $BrCH_2C\equiv CH$ at various molar ratios. Molar ratio: (a) 1 : 1.5–1.8 (EtOH), (b) 1 : 1 (EtOH), and (c) excess pyridine (H_2O). (Dashed lines) Bands recorded for highly concentrated solutions.

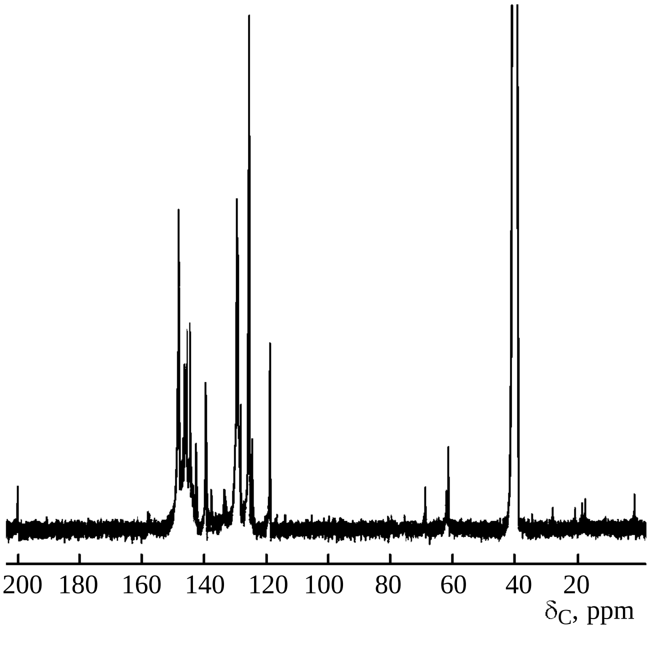
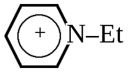
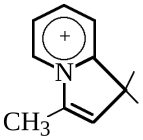
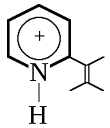
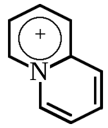


Fig. 4. ^{13}C NMR spectrum of the reaction product of pyridine with propargyl bromide (with excess pyridine).

Table 1. Long-wave absorption bands of certain heterocyclic cations containing a pyridine fragment

Cation	$\nu_{max}(H_2O)$	$\Delta\nu_{max}$
	38 500	0
	35 100[a]	3400[a]
	35 000[a]	0[a]
	30 900[b]	4100[b]
$C_5H_5N:BrCH_2C{\equiv}CH$ (~1 : 2)	30 100	8400[c]
$C_5H_5N:BrCH_2C{\equiv}CH$ (1 : 1)	30 100 27 500 23 000	8400[c] 11 000[c] 15 500[c]

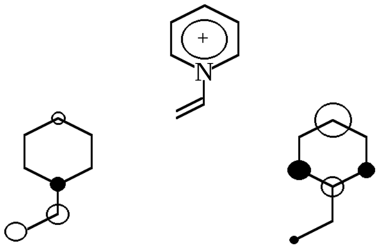
[a] Data of [7]. [b] Data of [8, 9]. [c] Relative to the *N*-ethylpyridinium cation.

carbon atoms. The signals at δ_C 56–68 ppm, assignable to >CHN and CH_2N carbons [13], comprise 5%. The spectrum contains a signal at δ_C 199.9 ppm, assignable to the allenic =C= carbon [13].

In view of the data in Table 2, the assigned quaternary, tertiary, secondary, and primary carbon signals, as well as the results of qualitative and quantitative analysis of the ^{13}C NMR specrum of the sample (Table 3), we came to the following conclusions concerning the chemical structure of the reaction products of pyridine with propargyl bromide. The major product is compound **VII** represented by several rotamers, which explains the observation in the spectrum of a great number of signals with close δ_C values. The signals of equal intensity at 199.9 (=C=) and 61.3 (CH_2N) ppm are likely to belong to compound **VI**. According to calculations, the fractions of compounds **VII** and V are 86 and 10 wt %, respectively, and 4 wt% fall at unidentified compounds. The theoretical elemental compositions of compounds **VI** and **VII** are consistent with experiment (Table 3).

Thus, the proposed structure of cation **VII** is consistent with all the experimental evidence. The shift of its UV absorption maximum with respect to those characteristic of *N*-alkyl cations is readily interpreted with the aid of HF/6-31G* nonempirical quantum-chemical calculations. Analysis of the structure of π-MOs (HOMO and LUMO) of the model *N*-vinylpyridinium cation points to strong mixing of the vinyl and pyridine fragment orbitals (Scheme 2). This result explains the low-frequency shift of the long-wave electronic transition of the vinylpyridinium cation (Figs. 1, 3).

Scheme 2.



HOMO
–14.19 eV

LUMO
–3.28 eV

EXPERIMENTAL

The ^{13}C NMR spectrum of the sample with proton decoupling and the subspectra of primary and tertiary

Table 2. Chemical shifts in the ^{13}C NMR spectra of pyridine and pyridinium cations

Compound	δ_C, ppm					
	$C^{2,6}$	$C^{3,5}$	C^4	C^α	C^β	C^γ
C_5H_5N[a]	150.2	123.9	135.9	–	–	–
$[C_5H_5N]^+H$[a]	142.4	129.0	148.3	–	–	–
$[C_5H_5NCH_2CH_3]^+Br^-$	144.4	127.9	145.3	55.9	16.2	–
$[C_5H_5NCH_2C{\equiv}CH]^+Br^-$	144.7	128.1	146.4	49.6	81.3	75.2

[a] Data of [12].

Table 3. Relative contents of carbon atoms in the reaction product of excess pyridine with propargyl bromide (in fractions q_x[a]) and its elemental composition (%) (parenthesized are calculated values)[b]

q_x	δ_C, ppm
0.006	199.9 (CH=*C*=CH)
0.120	146.0–148.0 (C^4 in pyridinium cations)
0.211	142.0–146.0 ($C^{2,6}$ in pyridinium cations)
0.221	127.0–129.0 ($C^{3,5}$ in pyridinium cations)
0.306	132.0–139.0, 124.0–125.5 [*C*H=*C*H]
0.006	61.3 (CH_2N)
0.130	118.7, 1.7–68.0 (unidentified compounds)

[a] Relative to the total integral intensity in the ^{13}C NMR spectrum, taken for 1. [b] C 48.72 (48.48); H 4.13 (4.04); Br 40.02 (40.40); N 7.40 (7.07).

and secondary and quaternary carbon atoms, obtained by the spin-echo technique with multiplet dephasing, [11], were registered on a Varian VXR-500S spectrometer (125.5 MHz, relaxation delay 2.5 s, pulse 90°) in DMSO-d_6. The relaxant was chromium trisacetylacetonate (*c* 0.02 M). Structural assignment from the ^{13}C NMR spectra was based on calculations, assuming the sum of the fractions of the $C^{2,6}$, $C^{3,4}$, and C^4 atoms of the pyridinium cations equal to five carbon atoms. Calculation of the fraction of each compound in the mixture (wt%) from the ^{13}C NMR spectrum was performed with the elemental compositions obtained by chemical methods. The fractions of compounds **VI** and **VII** were determined with a relative error of no higher than 7%. Nonempirical calculations of the geometry of cation **VI** in the HF/6-31G* basis and of its UV spectra were perfomed using GAUSSIAN 94 [14].

Rection of pyridine with propargyl bromide. *a*. Propargyl bromide, 2.38 g, was slowly added with stirring to a solution of 1.58 g of pyridine in 5 ml of absolute acetonitrile. Heat release was observed, and the reaction mixture got dark brown. The solvent was removed in a vacuum to leave a tarry noncrystallizing material, yield 3.96 g (100%).

b. Propargyl bromide, 4.76 g, was slowly added with stirring to a solution of 1.58 g of pyridine in 5 ml of absolute acetonitrile, and the resulting mixture was allowed to stir at 20°C for 4 h. The precipitate that formed was filtered off, washed on the filter with cold acetonitrile, and dried in a vacuum to obtain *N*-(2-propyn-1-yl)pyridinium bromide as a single product, yield 3.15 g (80% per pyridine), mp 122–124°C. Found, %: C 48.40; H 3.96; Br 40.38; N 6.90. C_8H_8BrN. Calculated, %: C 48.48; H 4.04; Br 40.40; N 7.07.

c. A solution of 2.38 g of propargyl bromide in 5 ml of absolute acetonitirile was added dropwise with stirring to 3.16 g of pyridine. The mixture warmed up to 50–55°C and got brown. It was stirred for 2 h at 20°C, and the solvent was removed in a vacuum to leave a glassy material (mp 149–151°C) which was a mixture of dimers **VI** and **VII** of *N*-(2-propyn-1-yl)pyridinum bromide (**II**). Yield 3.72 g (94% per propargyl bromide), soluble in water and ethanol. Found, %: C 48.72; H 4.13; Br 40.02; N 7.40. $C_{16}H_{16}Br_2N_2$. Calculated, %: C 48.48; H 4.04; Br 40.40; N 7.07.

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