105. The Synthesis and Reactions of 1-(2-Propynyl)pyridinium Salts

by Alan R. Katritzky*, Otto A. Schwarz and Olga Rubio

Department of Chemistry, University of Florida, Gainesville, Fl. 32611, U.S.A.

and Diether G. Markees

Department of Chemistry, Wells College, Aurora, N.Y. 13026, U.S.A.

(5.I.84)

Summary

The synthesis of 1-(2-propynyl)pyridinium salts 3 is described. Compounds 3 react with a second pyridine molecule, in the presence of the corresponding hydrochloride, to form products of type 4. Certain bases cause the 1-(2-propynyl)pyridinium salts 3 to rearrange into 1-propadienylpyridinium salts 5. Diethylamine converts compounds 3 into 1-acetonylpyridinium salts 8. Moreover, treatment of 3 or 5 with sodium metho-xide gives enol ethers of type 9, which can be hydrolyzed to the ketones 8. Addition of bromine to some of the unsaturated compounds is also reported.

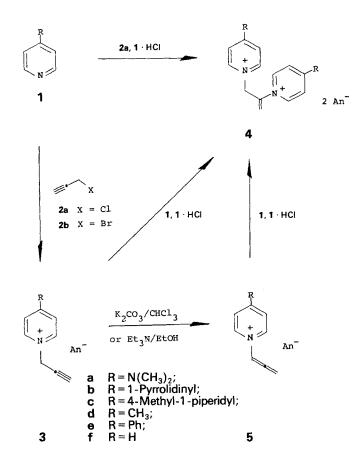
The chemistry of 1-vinyl- and 1-allyl-pyridinium salts has recently received more attention [1], but little is known about the 1-(1-propynyl) and 1-(2-propynyl) analogues. Reportedly, treatment of pyridine with 2-propynyl halides at 0 °C for 18 h gave the 1-(2-propynyl)pyridinium halide **3f** [2], while heating both reagents in a sealed tube for 15 h at 70 °C [3] or 30 h at 60 °C [4] afforded polymers of 1-(2-propenyl)pyridinium salts.

We have examined the reactions of several pyridines with these halides and found a significant influence of the 4-substituent on the course of the reaction. Pyridines with a strong electron-donor substituent in the 4-position 1a-c gave with 2-propynyl halides 2a or 2b the expected 1-(2-propynyl)pyridinium salts (3a-c) in high yields. γ -Picoline (1d) and 4-phenylpyridine (1e), however, are much less reactive and gave 3d and 3e only in moderate yields. The ¹H-NMR spectra of compounds 3a-e are characterized by a triplet near 2.8 ppm (in 3d at 2.95 ppm) and a doublet in the region 4.5-5.4 ppm due to the propynyl substituent. The coupling constants of 3 Hz agree with the expected value for a ⁴J coupling. The ¹³C-NMR spectra confirm structures 3 (Table 1).

Extending the reaction time between 1d and 2b to 12 h improved the yield of 3d. However, 4-phenylpyridine (1e) behaved differently. Nucleophilic attack of a second mole of 4-phenylpyridine (1e) converted initially formed 3e into the pyridinium halide 4e. Compound 4e was also obtained in high yield by refluxing 1e with 2-propynyl bromide (2b) in EtOH for 30 min. Treatment of pyridine 1f with the 2-propynyl halides 2a or 2b for 18 h either at 0°C or at 70°C gave a mixture shown spectroscopically to







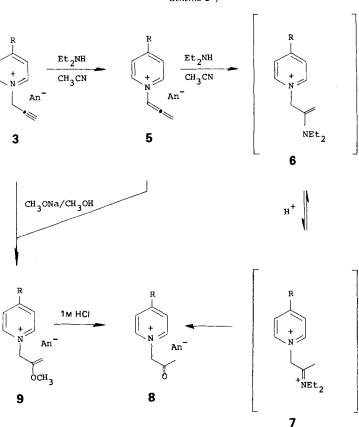
contain 4f rather than 3f. Moreover, when 2a reacted with pyridine in the presence of pyridine hydrochloride, pure 4f was formed. Product 4d was also obtained directly from 1d and 1d \cdot HCl, with 2a. However, preparation of 4a and 4b was only accomplished by treatment of 3a and 3b with the corresponding pyridine in the presence of equimolar amounts of 1a \cdot HCl and 1b \cdot HCl, respectively, which suppressed the formation of intractable polymeric by-products.

The structure assignment of compounds 4 is based on spectral evidence. In the ¹H-NMR spectrum the olefinic methylene protons appear as an *AB*-system in the region 5.7–6.2 ppm, while the *N*-methylene protons appear as a singlet (5.4–6.2 ppm). No allylic coupling is observed. Increasing the electron-donor character of the 4-substituent causes a diamagnetic shift of the A_2X_2 -system of the pyridine protons. The ¹³C-NMR spectra display a triplet and a singlet corresponding to the olefinic C-atoms and a triplet for the saturated methylene C-atom, thus confirming the structure of the C_3 -moiety. The α -, β -, and γ -C-atom of the two pyridine rings are nonequivalent and therefore give rise to six signals (*Table 1*).

(2)C(3) a -C β -C γ -C77.0 (s)73.1 (d)141.4 (d)107.9 (d)155.0 (s)73.5 (s)78.7 (d)141.4 (d)108.8 (d)155.9 (s)73.3 (s)78.7 (d)141.4 (d)108.8 (d)155.9 (s)73.3 (s)78.7 (d)141.4 (d)108.5 (d)155.9 (s)72.2 (s)80.1 (d)142.6 (d)129.2 (d)161.7 (s)72.2 (s)80.1 (d)143.5 (d)133.5 (d)159.4 (s)72.2 (s)80.1 (d)141.8 (d)108.1 (d)156.2 (s)72.2 (s)80.1 (d)141.8 (d)109.2 (d)156.2 (s)72.2 (s)119.4 (r)141.4 (d)109.2 (d)156.2 (s)72.2 (s)119.4 (r)141.4 (d)109.2 (d)156.4 (s)72.2 (s)123.6 (r)141.4 (d)109.2 (d)156.4 (s)42.9 (s)123.5 (d)130.1 (d)155.5 (s)142.1 (s)122.4 (r)144.2 (d)129.7 (d)158.8 (s)41.9 (s)122.4 (r)145.7 (d)129.7 (d)158.8 (s)00.7 (s)92.5 (r)138.7 (d)129.7 (d)155.3 (s)01.6 (s)92.1 (r)138.7 (d)129.7 (d)155.3 (s)01.6 (s)92.1 (r)138.7 (d)133.5 (d)155.3 (s)01.6 (s) <t< th=""><th>$\overline{C(1)}$ $\overline{C(2)}$ $\overline{C(3)}$ $\overline{C(3)}$ \overline{F}_{-C} \overline{F}_{-C}</th><th>Comp.</th><th>Anion</th><th>N(1) Substituent</th><th>uent</th><th></th><th>Pyridinium ring</th><th>ing</th><th></th><th>Pyridine-4-substituent</th></t<>	$\overline{C(1)}$ $\overline{C(2)}$ $\overline{C(3)}$ $\overline{C(3)}$ \overline{F}_{-C}	Comp.	Anion	N(1) Substituent	uent		Pyridinium ring	ing		Pyridine-4-substituent
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$			C(1)	C(2)	C(3)	a-C	β-C	γ-C	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	3a ^b)	Cl0 ⁷	45.7 (t)	77.0 (s)	79.1 (d)	141.4(d)	107.9 (d)	156.0 (s)	39.8 (q, N(CH ₃) ₂)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	Эр	CIO ⁻	46.8 (t)	73.6 (s)	78.4 (d)	140.7 (d)	108.8(d)	154.2 (s)	48.9 (t, CH ₂ NCH ₂); 24.9 (t, CH ₂ CH ₂)
Br 50.2 (t) 72.0 (s) 80.6 (d) 142.6 (d) 133.5 (d) 159.4 (s) ClO_4 57.0 (t) 142.7 (s) 117.9 (t) 143.5 (d) 133.5 (d) 159.4 (s) ClO_4 57.0 (t) 142.7 (s) 117.9 (t) 141.8 (d) 108.1 (d) 156.2 (s) ClO_4 57.0 (t) 142.7 (s) 117.9 (t) 141.4 (d) 109.2 (d) 156.4 (s) ClO_4 58.7 (t) 142.2 (s) 119.4 (t) 141.4 (d) 156.4 (s) 156.4 (s) ClO_7 58.5 (t) 142.2 (s) 119.4 (t) 141.4 (d) 156.3 (s) 154.3 (s) ClO_7 61.2 (t) 142.2 (s) 122.4 (t) 142.8 (d) 155.3 (d) 154.3 (s) ClO_7 60.2 (t) 141.9 (s) 122.4 (t) 142.8 (d) 159.3 (s) 154.3 (s) ClO_7 60.2 (t) 141.9 (s) 122.4 (t) 142.8 (d) 159.3 (d) 159.3 (s) ClO_7 62.3 (t) 142.8 (s) 125.5 (d) 125.3 (d) 159.3 (s) ClO_7	Br 50.2 (1) 72.0 (s) 80.6 (d) 142.6 (d) 133.5 (d) 161.7 (s) CIO_4 57.0 (t) 72.2 (s) 80.1 (d) 143.5 (d) 133.5 (d) 156.1 (s) CIO_4 57.0 (t) 142.9 (s) 11179 (t) 141.8 (d) 108.1 (d) 156.1 (s) CIO_4 57.0 (t) 142.9 (s) 1194.4 (t) 199.2 (d) 156.1 (s) CIO_4 58.5 (t) 142.9 (s) 1194.4 (t) 199.2 (d) 156.1 (s) CIO_4 61.2 (t) 142.9 (s) 1194.4 (t) 199.9 (d) 156.1 (s) CIO_4 61.2 (t) 142.9 (s) 123.4 (t) 199.2 (d) 154.3 (s) Br^- 60.2 (t) 141.9 (s) 122.4 (t) 142.8 (d) 153.3 (d) CIO_4 62.3 (t) 142.2 (s) 124.2 (t) 144.2 (d) 153.3 (d) Br^- 60.2 (t) 132.4 (t) 143.2 (d) 123.3 (d) 153.3 (d) Br^- 103.3 (d) 124.2 (t) 144.4 (d) 129.7 (d) 148.8 (d)	36	CIO ⁴	46.9 (t)	73.3 (s)	78.7 (d)	141.4(d)	108.5 (d)	155.9 (s)	47.9 (t, CH ₂ NCH ₂); 33.5 (t, CH ₂ CH ₂);
Br 502 (1) 72.0 (s) 80.6 (d) 142.6 (d) 129.2 (d) 161.7 (s) ClO_4 50.2 (t) 72.0 (s) 80.6 (d) 143.5 (d) 133.5 (d) 156.2 (s) ClO_4 57.0 (t) 142.7 (s) 117.9 (t) 141.8 (d) 108.1 (d) 156.2 (s) ClO_4 57.0 (t) 142.7 (s) 117.9 (t) 141.4 (d) 109.7 (d) 156.1 (s) ClO_4 58.5 (t) 142.9 (s) 119.4 (t) 139.9 (d) 109.2 (d) 154.3 (s) ClO_4 61.2 (t) 141.9 (s) 122.4 (t) 139.9 (d) 199.2 (d) 154.3 (s) ClO_4 61.2 (t) 141.9 (s) 122.4 (t) 144.2 (d) 129.2 (d) 154.3 (s) ClO_4 62.3 (t) 144.2 (d) 125.5 (d) 159.3 (s) 1 ClO_7 62.3 (t) 144.2 (d) 125.3 (d) 158.8 (s) 1 ClO_7 62.3 (t) 144.2 (d) 125.5 (d) 159.3 (s) 1 148.8 (d) ClO_7 62.3 (t) 142.8 (s)	Br 50.2 (1) 72.0 (s) 80.6 (d) 142.6 (d) 129.2 (d) 161.7 (s) CIO ₄ 57.0 (t) 72.2 (s) 80.1 (d) 143.5 (d) 133.5 (d) 156.1 (s) 1 CIO ₄ 57.0 (t) 142.7 (s) 117.9 (t) 141.8 (d) 108.1 (d) 156.1 (s) 156.1 (s) CIO ₄ 55.0 (t) 142.7 (s) 117.9 (t) 141.8 (d) 109.2 (d) 154.3 (s) 144.3 (s) CIO ₄ 58.5 (t) 142.2 (s) 123.6 (t) 141.4 (d) 199.2 (d) 154.3 (s) 144.3 (s) CIO ₄ 61.2 (t) 142.2 (s) 123.4 (t) 142.5 (d) 159.3 (s) 144.3 (s) CIO ₄ 62.3 (t) 142.2 (s) 123.8 (d) 148.8 (d) 148.8 (d) CIO ₄ 62.3 (t) 142.8 (s) 129.3 (d) 155.3 (d) 155.3 (d) 155.3 (d) 155.3 (d) 155.3 (d) 155.3 (d) 148.8 (d) CIO ₄ 62.3 (t) 142.2 (t) 145.5 (d) 129.3 (d) 148.8 (d) 169.3 (s) 160.2 (d) 155.3									30.68 (d, CH-); 20.5 (q, CH ₃)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	3d	Br ⁻	50.2 (1)	72.0 (s)	80.6 (d)	142.6 (d)	129.2 (d)	161.7 (s)	21.5 (t, CH ₃)
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	3 e	CIO ⁷	50.2 (t)	72.2 (s)	80.1 (d)	143.5(d)	133.5(d)	159.4 (s)	133.4 (s, C(1)); 130.3 (d, C(2));
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $									125.5 (d, C(3)); 128.5 (d, C(4))
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	4 a ^b)	CIO_4^-	57.0 (t)	142.7 (s)	(1) (1)	141.8 (d)	108.1 (d)	156.2 (s)	$40.1 \ (q, -N(CH_3)_2)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						140.2 (d)	107.7 (d)	156.1 (s)	$39.8 (q, -N(CH_3)_2)$
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4	CIO ⁷	58.5 (t)	142.9 (s)	119.4 (t)	141.4 (d)	109.2(d)	154.5 (s)	49.3 (t, CH_2NCH_2);
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						139.9 (d)	109.2 (d)	154.3 (s)	49.1 (t, CH ₂ NCH ₂); 24.8 (t, CH ₂ CH ₂)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Br ⁻ 60.2 (t) 141.9 (s) 122.4 (t) 142.8 (d) 129.8 (d) 163.5 (s) 1 CIO ₄ 62.3 (t) 141.9 (s) 122.4 (t) 145.7 (d) 125.5 (d) 1593.3 (s) 1 CIO ₄ 62.3 (t) 142.8 (s) 124.4 (t) 125.5 (d) 1593.3 (s) 1 CIO ₄ 62.3 (t) 142.8 (s) 124.4 (d) 129.7 (d) 148.8 (d) 1 CIO ₄ 103.3 (d) 200.7 (s) 92.5 (t) 138.5 (d) 168.3 (d) 155.9 (s) 1 CIO ₄ 103.2 (d) 201.6 (s) 92.0 (t) 138.7 (d) 108.7 (d) 155.3 (s) 1 CIO ₄ 103.2 (d) 201.6 (s) 92.0 (t) 138.7 (d) 108.7 (d) 155.3 (s) 1 CIO ₄ 105.1 (d) 202.9 (s) 93.4 (t) 140.1 (d) 129.2 (d) 155.3 (s) 1 1 CIO ₄ 65.0 (t) 202.9 (s) 93.7 (t) 140.1 (d) 129.2 (d) 155.3 (s) 1 1 CIO ₄ 65.0 (t	4d	CIO_4^-	61.2 (1)	142.2 (s)	123.6 (t)	144.2 (d)	130.1 (d)	164.3(s)	21.9 (q, CH ₃)
$ \begin{array}{llllllllllllllllllllllllllllllllllll$	Br ⁻ 60.2 (t) 141.9 (s) 122.4 (t) 145.7 (d) 125.5 (d) 159.3 (s) 1 ClO ₄ 62.3 (t) 144.9 (s) 124.2 (t) 144.5 (d) 125.3 (d) 158.8 (s) 1 ClO ₄ 62.3 (t) 142.8 (s) 124.2 (t) 144.5 (d) 129.7 (d) 148.8 (d) 1 ClO ₄ 103.3 (d) 200.7 (s) 92.5 (t) 138.5 (d) 108.1 (d) 155.3 (s) 1 1 ClO ₄ 103.3 (d) 200.7 (s) 92.5 (t) 138.3 (d) 108.1 (d) 155.3 (s) 1 1 ClO ₄ 103.2 (d) 201.6 (s) 92.0 (t) 138.7 (d) 169.2 (d) 155.3 (s) 1 ClO ₄ 103.2 (d) 202.9 (s) 93.4 (t) 140.1 (d) 129.2 (d) 155.3 (s) 1 ClO ₄ 105.8 (d) 203.2 (s) 93.7 (t) 140.9 (d) 155.3 (s) 1 1 ClO ₄ 65.0 (t) 203.2 (s) 93.7 (t) 140.9 (d) 155.3 (s) 1 1						142.8 (d)	129.8 (d)	163.5 (s)	$21.8 (q, CH_3)$
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4 e	Br	60.2 (t)	141.9 (s)	122.4 (t)	145.7 (d)	125.5 (d)	159.3 (s)	133.4 (d); 133.3 (d); 132.8 (s);
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						144.2 (d)	125.3 (d)	158.8 (s)	130.0 (d); 128.1 (d)
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4f	Cl0 ⁷	62.3 (t)	142.8 (s)	124.2 (t)	145.5 (d)	130.0(d)	148.8 (d)	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$						$144.4 \ (d)$	129.7 (d)	148.3 (d)	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	5a ^b)	CIO_{4}^{-}	103.3 (d)	200.7 (s)	92.5 (1)	138.5 (d)	108.1 (d)	155.9 (s)	39.9 $(q, N(CH_3)_2)$
Br ⁻ 103.2 (d) 201.6 (s) 92.0 (t) 138.7 (d) 108.2 (d) 155.3 (s) CIO ₄ 105.1 (d) 202.9 (s) 93.4 (t) 140.1 (d) 129.2 (d) 161.1 (s) 1 CIO ₄ 105.8 (d) 203.2 (s) 93.7 (t) 140.9 (d) 133.5 (d) 158.7 (s) 1 CIO ₄ 65.0 (t) 205.5 (s) 26.3 (q) 142.6 (d) 107.6 (d) 156.8 (s) 1 CIO ₄ 65.0 (t) 205.5 (s) 26.1 (q) 142.3 (d) 107.6 (d) 155.6 (s) 1 CIO ₄ 64.9 (t) 205.6 (s) 26.4 (q) 143.0 (d) 107.9 (d) 155.6 (s)	Br ⁻ 103.2 (d) 201.6 (s) 92.0 (t) 138.7 (d) 108.2 (d) 155.3 (s) ClO_4^{-} 105.1 (d) 202.9 (s) 93.4 (t) 140.1 (d) 129.2 (d) 161.1 (s) 1 ClO_4^{-} 105.1 (d) 202.9 (s) 93.7 (t) 140.9 (d) 133.5 (d) 158.7 (s) 1 ClO_4^{-} 105.8 (d) 203.2 (s) 93.7 (t) 140.9 (d) 133.5 (d) 158.7 (s) 1 ClO_4^{-} 65.0 (t) 205.5 (s) 26.3 (q) 142.6 (d) 107.6 (d) 156.8 (s) 1 ClO_4^{-} 64.9 (t) 205.8 (s) 26.1 (q) 142.3 (d) 107.9 (d) 154.0 (s) ClO_4^{-} 64.9 (t) 205.6 (s) 26.4 (q) 143.0 (d) 107.9 (d) 155.6 (s) In CDC1 ₃ /CF ₃ /COH referenced to CDC1 ₃ (77.0 ppm) except where otherwise stated; chemical shift (<i>b</i>) in ppm. In D ₀ ,DMSO referenced to (D ₀ ,DMSO (39.5 ppm). In D ₀ ,DMSO referenced to (D ₀ ,DMSO (39.5 ppm). In D ₀ ,DMSO referenced to (D ₀ ,DMSO (39.5 ppm). In D ₀ ,DMSO referenced to (D ₀ ,DMSO (39.5 ppm). In D ₀ ,DMSO referenced to (D ₀ ,DMSO (39.5 ppm). In D ₀ ,DMSO referenced to	Sb	C10 ⁻	103.5 (d)	201.6(s)	92.1 (t)	138.3 (d)	108.7 (d)	153.8 (s)	48.9 (t, CH ₂ NCH ₂); 24.8 (t, CH ₂ CH ₂)
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	5c	Br-	103.2 (d)	201.6 (s)	92.0 (t)	138.7 (d)	108.2 (d)	155.3 (s)	47.7 (t, CH ₂ NCH ₂); 33.3 (t, CH ₂ CH ₂);
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$									30.3 (d, CH); 20.5 (q, CH ₃)
CIO_4^- 105.8 (d) 203.2 (s) 93.7 (t) 140.9 (d) 133.5 (d) 158.7 (s) 1 CIO_4^- 65.0 (t) 205.5 (s) 26.3 (q) 142.6 (d) 107.6 (d) 156.8 (s) 1 CIO_4^- 64.9 (t) 205.5 (s) 26.1 (q) 142.3 (d) 107.6 (d) 154.0 (s) CIO_4^- 64.9 (t) 205.6 (s) 26.4 (q) 143.0 (d) 107.9 (d) 155.6 (s)	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	5d	CIO ¹	105.1 (d)	202.9 (s)	93.4 (t)	140.1 (d)	129.2 (d)	161.1 (s)	21.6 (q, CH ₃)
$CIO_{4}^{-} \qquad 65.0 (t) \qquad 205.5 (s) \qquad 26.3 (q) \qquad 142.6 (d) \qquad 107.6 (d) \qquad 156.8 (s) \\ CIO_{4}^{-} \qquad 64.9 (t) \qquad 205.8 (s) \qquad 26.1 (q) \qquad 142.3 (d) \qquad 108.2 (d) \qquad 154.0 (s) \\ CIO_{4}^{-} \qquad 64.9 (t) \qquad 205.6 (s) \qquad 26.4 (q) \qquad 143.0 (d) \qquad 107.9 (d) \qquad 155.6 (s) \\ \end{array}$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	5e	C10 ⁷	105.8 (d)	203.2 (s)	93.7 (t)	140.9 (d)	133.5 (d)	158.7 (s)	133.1 (s, C(1)); 130.3 (d, C(2));
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccc} CIO_4^{-} & 65.0 \ (t) & 205.5 \ (s) & 26.3 \ (q) & 142.6 \ (d) & 107.6 \ (d) & 156.8 \ (s) \\ CIO_4^{-} & 64.9 \ (t) & 205.8 \ (s) & 26.1 \ (q) & 142.3 \ (d) & 108.2 \ (d) & 154.0 \ (s) \\ CIO_4^{-} & 64.9 \ (t) & 205.6 \ (s) & 26.4 \ (q) & 143.0 \ (d) & 107.9 \ (d) & 155.6 \ (s) \\ \end{array}$									128.1 (d, C(3)); 125.4 (d, C(4))
CIO_4^- 64.9 (t) 205.8 (s) 26.1 (q) 142.3 (d) 108.2 (d) 154.0 (s) CIO_4^- 64.9 (t) 205.6 (s) 26.4 (q) 143.0 (d) 107.9 (d) 155.6 (s)	$\begin{array}{cccccccc} CIO_4^{-} & 64.9 (t) & 205.8 (s) & 26.1 (q) & 142.3 (d) & 108.2 (d) & 154.0 (s) \\ CIO_4^{-} & 64.9 (t) & 205.6 (s) & 26.4 (q) & 143.0 (d) & 107.9 (d) & 155.6 (s) \\ \end{array}$ $\begin{array}{cccccccccccccccccccccccccccccccccccc$	8a	CIO_{4}^{-}	65.0 (t)	205.5 (s)	26.3 (q)	142.6 (d)	107.6 (d)	156.8 (s)	39.7 (q, N(CH ₃) ₂)
CIO_4^- 64.9 (t) 205.6 (s) 26.4 (q) 143.0 (d) 107.9 (d) 155.6 (s) 47.7 (t, CH_2NCH_2); 33.4 (t, 33.4 (t, 30.5 (d, CH); 20.5 (d, CH_3)	$CIO_{4}^{-} 64.9 (t) 205.6 (s) 26.4 (q) 143.0 (d) 107.9 (d) 155.6 (s) 47.7 (t, CH2NCH2); 33.4 (t, CH2) CF3(C) + CCI3(CF3) + CCI3(CF3) + CCI3(CF3) + CCI3(T1, CF3) + CCI3 + CCI3) + CCI3(T1, CF3) + CCI3 + CCI3 + CCI3) + CCI3(T1, CF3) + CCI3 + CCI3 + CCI3) + CCI3(T1, CF3) + CCI3 + CCI3 + CCI3) + CCI3 + CCI3 + CCI3 + CCI3) + CCI3 + CCI3 + CCI3 + CCI3 + CCI3 + CCI3) + CCI3 + CCI3$	8 b	CIO_{4}^{-}	(t) (t)	205.8 (s)	26.1 (q)	142.3 (d)	108.2 (d)	154.0 (s)	48.6 (t, CH ₂ NCH ₂); 24.4 (t, CH ₂ CH ₂)
30.5 (d, CH); 20.5 (q, CH ₃)		8c	CIO_{4}^{-}	64.9 (t)	205.6 (s)	26.4 (q)	143.0 (d)	107.9 (d)	155.6 (s)	47.7 (t, CH ₂ NCH ₂); 33.4 (t, CH ₂ C);
	^a) In CDCl ₃ /CF ₃ COOH referenced to CDCl ₃ (77.0 ppm) except where otherwise stated; chemical shift (δ) in ppm. ^b) In (D ₆)DMSO referenced to (D ₆)DMSO (39.5 ppm).									30.5 (d, CH); 20.5 (q, CH ₃)
) II (q	D _k)DMSO rei	ferenced to (D,)]	DMSO (39.5 ppi	n).				

Helvetica Chimica Acta – Vol. 67 (1984)







a)

On exposure to bases, e.g. K_2CO_3 or Et_3N , the 1-(2-propynyl)pyridinium salts 3a-e rearranged to 1-propadienylpyridinium salts 5a-e. The rearrangement was indicated by the ¹H-NMR spectra, which exhibit a triplet in the region 7.0–7.5 ppm and a doublet near 6 ppm with characteristic allenic coupling ($^4J = 6$ Hz). The ¹³C-NMR spectra confirm this structure with a signal which is characteristic for sp-allenic C-atoms (cf. Table 5). This type of N-(2-propynyl) to N-allenyl rearrangement has been reported previously for *neutral* heterocyclic systems as acridones [5], carbazoles [6], and pyrazoles [7]. The only cationic example is a proposed intermediate in the benzimidazole series [8]. Presumably, these allenyl salts 5 are intermediates in the conversion of 1 or 3, respectively, to 4, because 5a and 5b have also been successfully transformed into the corresponding bis-pyridiniopropene salts 4a and 4b. Various attempts to induce further isomerization of 5 to give 1-(1-propynyl)pyridinium salts failed: decomposition occurred on contact with stronger bases (e.g. KOH).

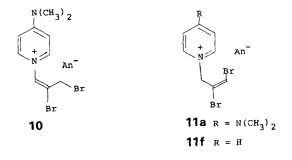
Treatment of 5a-c with Et_2NH in refluxing EtOH or CH_3CN led to the formation of 1-acetonylpyridinium salts 8a-c, which were also obtained from the corresponding



1-(2-propynyl)pyridinium salts 3 without isolation of the allenic intermediate. The ¹H-NMR spectra contain two singlets at about 5.2 and 2.4 ppm representing the H-atoms contained in the acetonyl group. The ¹³C-NMR spectra are also consistent with the suggested structure 8 (*Table 1*). The reaction of **5a**-**c** with Et₂NH leads via 6 to the iminium salts 7, which are subsequently hydrolyzed to the ketones 8. The high yields in the sequence $1\rightarrow 3\rightarrow 8$ provide a new, efficient access to these ketones, avoiding the use of lachrymatory α -halo ketones.

Treatment of 3a and 3b with CH₃ONa/CH₃OH at room temperature led to the 1-(2-methoxy-2-propenyl)pyridinium salts 9a and 9b, respectively. Since the reaction of 5a and 5b under similar conditions also furnished the enol ethers 9a and 9b, respectively; it is likely that the 1-(2-propynyl)pyridinium cations rearrange into the corresponding allenes prior to nucleophilic attack. The ¹³C-NMR spectra of compounds 9 confirm the structure of the *N*-substituent. Chemical evidence for the formation of the enol ethers 9a and 9b was provided by their acid hydrolysis to the ketones 8a and 8b.

Although the 1-vinylpyridinium cation does not react with Br_2 at room temperature [9], 4-dimethylamino-1-vinylpyridinium bromide [1] gave the expected 1-(1,2-dibromoethyl)-4-(dimethylamino)pyridinium salt on warming in CHCl₃/EtOH solution [10]. When 1-propadienylpyridinium salt **5a** was allowed to react with Br_2 , only the terminal double bond was attacked to yield (*E*)-1-(2,3-dibromo-1-propenyl)-4-(dimethylamino)pyridinium perchlorate (**10**). The structure of **10** was established by ¹³C-NMR spectroscopy, which showed, besides a triplet at 60.7 ppm (BrCH₂), a doublet at 110.7 ppm and a singlet at 116.8 ppm, assigned to the olefinic C-atoms. Measurement of the Nuclear *Overhauser* Effect showed a significant enhancement of the signal of the aromatic α -protons on irradiating the aliphatic methylene protons, thus confirming the (*E*)-configuration of the double bond in **10**. Treatment of the 1-(2-propynyl)pyridinium salt **3a** with bromine furnished 1-(2,3-dibromo-2-propenyl)-4-(dimethylamino)pyridinium salt (**11a**). A similar reaction of **3f**, leading to **11f**, has been reported previously [2].



We thank the *Kulturamt der Stadt Wien* for a grant (to O.A.S.), the Institute of Pharmaceutical Chemistry, University of Vienna, for leave of absence (to O.A.S.), and the Instrument Program, Chemistry Division, National Science Foundation for a grant for *Nicolet NT-300* spectrometer (at University of Florida).

Experimental Part

General. Melting points (m.p.) were determined on a hot-stage apparatus and are uncorrected. ¹H-NMR spectra were recorded on a Varian EM-360L spectrometer (60 MHz) with TMS [δ (ppm) = 0] as internal standard and ¹³C-NMR spectra on a JEOL-FX 100 (25 MHz) (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet). NOE measurements were done with a Nicolet NT-300 spectrometer. The 2-propynyl bromide was used as 80% solution in toluene. Solvents were removed in vacuo (20 mm Hg). Anion exchange was effected by adding NaClO₄ (50%, 1.3 equiv.) to the bromide salt (1 equiv.) in EtOH; the perchlorate crystallized on standing at 25°.

General Procedure for the Synthesis of 4-Substituted 1-(2-Propynyl)pyridinium Salts 3. A solution of 1 (10 mmol) in CH₂Cl₂ (5-20 ml) was added dropwise to the stirred 2-propynyl halide (10 mmol) at r.t. Stirring was continued for the time given in Table 1. The precipitate was filtered off and washed with Et₂O. In the case of 3a, b and e, the hygroscopic halides were converted into the perchlorates before recrystallization (Table 2).

Com-	Anion	Time	Yield	Recrystal-	M.p.	Formula	M.W.	Calc.	[%]		Found	1 [%]	
pound		[h]	[%]	lization solvent	[°C]			C	H	N	C	Н	N
3a	ClO ₄	1	82 ^a)	EtOH	150-151	C ₁₀ H ₁₃ ClN ₂ O ₄	260.7	46.07	5.02	10.75	45.89	5.15	10.6
3b	ClO ₄	0.5	95	EtOH	127	$C_{12}H_{15}ClN_2O_4$	286.7	50.27	5.27	9.77	50.41	5.38	9.6
3c	Br	1	95	CH ₃ CN	167-169	C ₁₄ H ₁₉ BrN ₂	295.2	56.94	6.44	9.49	56.61	6.52	9.2
3d	Br-	12 ^b)	70	EtOH/ Et ₂ O	177-179	C ₉ H ₁₀ BrN	212.1	50.37	4.75	6.60	50.73	4.73	6.4
3e	ClO ₄	1	48	EtOH/ H ₂ O	126–132	C ₁₄ H ₁₂ CINO ₄ + ½ H ₂ O	302.7	55.55	4.32	4.63	55.25	3.98	4.4

Table 2. Preparative and Analytical Data for 1-(2-Propynyl)pyridinium Salts 3

Procedures for the Synthesis of Pyridinio Halides 4. – Method A. A mixture of 2a (0.7 g, 10 mmol), 1 (10 mmol) and 1 · HCl (10 mmol) in CH₃CN (20 ml) was refluxed for the time indicated in *Table 4*. After cooling, the precipitated crystals were filtered off and converted into the perchlorate for recrystallization.

Method B. A mixture of 3 or 5 (5 mmol), free base 1 (5 mmol) and $1 \cdot \text{HCl}$ (5 mmol) in EtOH (10 ml) was refluxed for 3 h. After removal of the solvent, the remaining solid was washed carefully with acetone. The hygroscopic $4 \cdot$ halides were transformed into the perchlorates before recrystallization.

Method C. A mixture of 1e (1.55 g, 10 mmol) and 2b (1.61 g, 10 mmol) in EtOH (20 ml) was refluxed for 30 min. The precipitated solid was filtered off, washed with Et_2O and recrystallized. Additional preparative and analytical information is contained in *Table 3*.

Procedures for the Rearrangement of 3 into 4-Substituted 1-Propadienylpyridinium Salts 5. – Method A. A solution of 3 (10 mmol) in EtOH (10 ml) was stirred at r.t. for 2.5 h in the presence of Et_3N (1.1 ml, 8 mmol). The solvent was removed and the remaining residue washed with Et_2O and converted to the perchlorate (except 5c) for further purification.

Method B. A solution of 3 (5 mmol) in CHCl₃ (40 ml) or CH₂Cl₂/EtOH (1:1, 40 ml) was stirred at r.t. in the presence of anh. K_2CO_3 (2.7 g, 20 mmol) for 2 h. The inorganic salt was filtered off. Workup as in Method A gave 5. For additional preparative information and analyses see Table 4.

Procedures for the Conversion of 3 or 5 into 4-Substituted 1-Acetonylpyridinium Salts 8. – Method A. A solution of 3 or 5 (5 mmol) in CH₃CN (25 ml) or EtOH (20 ml) was refluxed with Et₂NH (0.44 g, 6 mmol) for 3 h. After removal of the solvent, the brownish oily residue was crystallized by stirring with Et₂O. The solid was collected and converted into the perchlorate for recrystallization (*Table 5*).

Method B. Compounds 9a or 9b (5 mmol) were dissolved in HCl (20 ml, 1M) and stirred for 2 h at r.t. After concentration of the solution, the pyridinium halides 8a and 8b were precipitated by addition of Et_2O , filtered and converted into the perchlorates for recrystallization. For additional preparative information and analyses see Table 5.

	1			1			Table 3. P1	Table 3. Preparative and Analytical Data for Salts 4	nalytical D	ata for Salts	s 4					
$ \begin{array}{ c c c c c c c c c c c c c c c c c c c$	Com-		Meth-		Yield	Recrystal-	M.p.	Formula			Calc. [%	[]		Found	[%]	
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	punod		od ^a)	[4]	[%]	lization solvent	[c]		!		0	Н	z	C	H	z
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	4a	CI0 ⁻	B	3	58	EtOH	236-238	C ₁₇ H ₂₄ Cl ₂ N			42.25	5.01	11.59	42.14	4.84	11.26
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	4	Cl07	B	3	78	CH ₃ CN		$C_{21}H_{28}Cl_2N$			47.12	5.26	10.46	47.32	5.29	10.58
	4 d	CIO_{4}^{-}	A	23	64°)	EtOH/H ₂ O		C ₁₅ H ₁₈ Cl ₂ N			42.37	4.27	6.59	42.47	4.41	6.49
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	4e	Br~	С	0.5	90	EtOH/	271-273	$C_{25}H_{22}Br_2N$			58.85	4.34	5.49	58.58	4.31	5.13
or Method: A. B and C see Exper. Part. Identified of crude chloride, characterized as the ClO _T salt. Table A. Preparative and Analytical Data for 1. Propadienty/pyridintium Salts S Anion Method ¹) Yield Recrystal. M.p. Found ($[c_0]$) Anion Method ¹) Yield Recrystal. M.p. Found ($[c_0]$) Found ($[c_0]$) Anion Method ¹) Yield Recrystal. M.p. Found ($[c_0]$) Found ($[c_0]$) Found ($[c_0]$) Anion Method ¹) Yield Recrystal. M.p. Found ($[c_0]$) Found ($[c_0]$) Found ($[c_0]$) Found ($[c_0]$) Albe 96< EtoH1 134-126 Cl ₀ H ₁₉ ClNO ₄ 260.7 46.07 5.31 10 Method ¹ Number of Close Cl ₀ H ₁₉ ClNO ₄ 260.7 46.07 5.31 10 Albe 95 <etoh1< th=""> 1041-143 Cl₀H₁₉ClNO₄ 286.7 9.21 6.17 6.19 6.17 6.19 6.17 6.19 7 6.17</etoh1<>	4f	CIO_4^-	A	19	52 ^b)	CH ₃ CN EtOH/H ₂ O		C ₁₃ H ₁₄ Cl ₂ N			39.31	3.55	7.06	39.25	3.54	6.87
Table 4. Preparative and Analytical Data for 1-Propadienty/pridnium Salts 5 Anion Method ⁴) Yield Recrystal-M.p. Formula M.W. Calc. [%] Found [%] Found [%] Anion Method ⁴) Yield Recrystal-M.p. Formula M.W. Calc. [%] Found [%] N ClO ₇ A/B 95 EtOH 141-143 Cn ₀ H ₁₉ ClN ₂ O ₄ 260.7 46.07 50.27 9.17 56.93 5.31 1 ClO ₇ A/B 95 EtOH 157-160 Cn ₁ H ₁₉ BrN ₂ 235.2 56.94 6.44 9.49 57.06 6.31 352 ClO ₇ B 9 EtOH 155-162 Cn ₁ H ₁₉ BrN ₂ 235.2 56.94 6.43 9.49 57.06 6.44 9.49 57.06 6.44 9.49 57.06 6.44 9.49 57.06 6.44 9.45 57.96 6.44 9.49 57.06 6.44 9.45 57.96 6.44 9.45 57.96 6.45 4.57 <td></td> <td>or Methoa ield of cru</td> <td>ls A, B an de chloric</td> <td>d C see I</td> <td>Exper. Pt</td> <td><i>urt</i>. is the ClO₄ sa</td> <td>lt.</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>		or Methoa ield of cru	ls A, B an de chloric	d C see I	Exper. Pt	<i>urt</i> . is the ClO ₄ sa	lt.									
Anion Method* Yield Recrystal. M.p. Formula M.W. Calc. [%] Found [%] Found [%] $[96]$ lization [C] H N C H N C H N $[96]$ lization [C] EtoH 141-143 $C_{10}H_{13}CIN_{2}0_{4}$ 260.7 46.07 5.02 10.75 46.09 5.31 11 10 C H N C <td< th=""><th></th><th></th><th></th><th></th><th></th><th>Table 4. Pre</th><th>parative an</th><th>d Analytical Dat</th><th>a for 1-Pro</th><th>padienylpyri</th><th>idinium .</th><th>Salts 5</th><th></th><th></th><th></th><th></th></td<>						Table 4. Pre	parative an	d Analytical Dat	a for 1-Pro	padienylpyri	idinium .	Salts 5				
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	Com-		Methc					Formula	M.W.		[%]			Found [9	[0]	
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	punod			[%]		_				C	4	H	z	С	Н	z
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	5a	CIO ₄	A/B	96	EtC			C ₁₀ H ₁₃ CIN ₂ O ₄	260.7			.02	10.75	46.09	5.31	10.66
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	5b	CI07	A/B	95	EtC			C ₁₂ H ₁₅ CIN ₂ O ₄	286.7			5.27	9.77	50.23	5.14	9.50
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	<u>5</u>	Br '	A/B	95	EC E			C ₁₄ H ₁₉ BrN ₂	295.2			44.	9.49	57.06	6.64	9.70
OUA B 95 EUOH 135-162 C14H_2CINO4 293.1 57.25 4.12 4.77 56.91 3.92 4.12 In Methods A and B see Exper. Part. Table 5. Preparative and Physical Data for 1-Acetonylpyridinium Perchlorates B Method ^a) Yield Recrystal- M.p. Formula M.W. Calc. [%] Found [%] Method ^a) Yield Recrystal- M.p. Formula M.W. Calc. [%] N C H N No 75 EtOH/ 154-156 C10H_15CIN_2O_5 278.7 43.09 5.43 10.05 43.44 5.74 1 A 75 EtOH/ 154-156 C10H_15CIN_2O_5 278.7 43.09 5.43 10.05 43.44 5.74 1 B 95 EtOH 150-152 C12H_17CIN_2O_5 304.7 47.29 5.62 9.19 46.94 5.73 B 95 EtOH 167-170 C14H_21CIN_2O_5 332.7 50.53 6.36 8.42 50.89 6.56	א מי		n 1	8 8		•	-	C ₉ H ₁₀ CINO ₄	231.6			1.35	6.05	46.29	4.57	6.03
Northoods A and B see Exper. Part. Table 5. Preparative and Physical Data for 1-Acetonylpyridinium Perchlorates 8 Method ^a) Yield Recrystal- M.p. Formula M.W. Calc. [%] Found [%] Method ^a) Yield Recrystal- M.p. Formula M.W. Calc. [%] Found [%] Method ^a) Yield Ization [°C] M.P. Calc. [%] N C H N A 75 EtOH/ 154-156 Cl ₀ H ₁₅ CIN ₂ O ₅ 278.7 43.09 5.43 10.05 43.44 5.74 1 B 95 EtOH 150-152 Cl ₂ H ₁₇ CIN ₂ O ₅ 304.7 47.29 5.62 9.19 46.94 5.73 B 95 EtOH 167-170 Cl ₄ H ₂₁ CIN ₂ O ₅ 332.7 50.53 6.36 8.42 50.89 6.56		CI04	-	56	HE			C ₁₄ H ₁₂ CINO ₄	293.7			1.12	4.77	56.91	3.92	4.77
$ \begin{array}{c c c c c c c c c c c c c c c c c c c $	^a) F(Dr Method	s A and b		er. Part.											
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$					1-4	Lable 5. Prep.	arative and	Physical Data fo	or I-Aceton	ylpyridiniun	n Perchla	orates 8				
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	Com-		d ^a) Yield	Recry	ystal-	M.p.	Formul		И.W.	Calc. [%]				Found [%]		
A 75 EtOH/ 134-156 $C_{10}H_{15}CIN_2O_5$ 278.7 43.09 5.43 10.05 43.44 5.74 1 B 95 Et_5CO $C_{10}H_{15}CIN_2O_5$ 304.7 47.29 5.62 9.19 46.94 5.73 A 90 EtOH 150-152 $C_{12}H_{17}CIN_2O_5$ 304.7 47.29 5.62 9.19 46.94 5.73 B 95 EtOH 167-170 $C_{14}H_{21}CIN_2O_5$ 332.7 50.53 6.36 8.42 50.89 6.56 For Methods A and B see Exper. Part. For Methods A and B see Exper. Part.	punod		[%]	lizatio solvei	on nt	[.c]				C C	Н	z		С	Н	z
A 90 EtOH 150-152 C ₁₂ H ₁₇ ClN ₂ O ₅ 304.7 47.29 5.62 9.19 46.94 5.73 B 95 EtOH 167-170 C ₁₄ H ₂₁ ClN ₂ O ₅ 332.7 50.53 6.36 8.42 50.89 6.56 For Methods A and B see Exper. Part.	88	V R	75 05	EtOF) T	154-156	C ₁₀ H ₁₅ (:78.7	43.09	5.43	10.		43.44	5.74	10.04
A 90 EtOH 167-170 C ₁₄ H ₂₁ ClN ₂ O ₅ 332.7 50.53 6.36 8.42 50.89 6.56 For Methods A and B see Exper. Part.	8b	a < m	88	EtOF		150-152	C ₁₂ H ₁₇ (104.7	47.29	5.62	.6		46.94	5.73	9.01
Exper. Part.	8c	e e	8	EtOH	I	167-170	C ₁₄ H ₂₁ (32.7	50.53	6.36	×	42	50.89	6.56	8.35
	^a) (^b	or Method	A and H		er Part											

Helvetica Chimica Acta – Vol. 67 (1984)

945

General Procedure for the Synthesis of the 4-Substituted 1-(2-Methoxypropenyl)pyridinium Perchlorates 9. Compound 3 or 5 (5 mmol) was added to a solution of CH_3ONa in CH_3OH (prepared from 5 mmol of Na in 20 ml of MeOH) and stirred for 5 h at r.t. After removal of the solvent, the remaining 9 halides were converted into the perchlorates and recrystallized from MeOH.

l-(2-Methoxy-2-propenyl)-4-(dimethylamino)pyridinium Perchlorate (9a). Yield: 1.4 g (98%) 9a · perchlorate as white prisms, m.p. 133^a. ¹H-NMR ((D₆)DMSO): 3.35 (s, 6H, N(CH₃)₂); 3.60 (s, 3H, CH₃O); 4.40 and 4.50 (*AB*-system, $J_{AB} = 2$, 2H, =CH₂); 4.95 (s, 2H, CH₂); 7.20 and 8.45 (A_2X_2 -system, $J_{AX} = 8$, 4H, aromat. H). ¹³C-NMR ((D₆)DMSO): 39.7 (q, N(CH₃)₂)); 55.3 (q, CH₃O); 58.7 (t, NCH₂); 86.6 (t, =CH₂); 107.6 (d, pyridinium β-C); 142.0 (d, pyridinium α-C); 155.9 (s, =COCH₃); 156.8 (s, pyridinium α-C). Anal. calc. for C₁₁H₁₇ClN₂O₅ (302.6): C 45.14, H 5.85, N 9.57; found: C 44.84, H 5.79, N 9.45.

l-(2-Methoxy-2-propenyl)-4-(1-pyrrolidinyl)pyridinium Perchlorate (**9b**). Yield: 1.5 g (95%) **9b** · perchlorate as white prisms, m.p. 118–119°. ¹H-NMR ((D₆)DMSO): 2.10 (m, 4H, CH₂CH₂); 3.55 (m, 4H, CH₂NCH₂); 3.60 (s, 3H, OCH₃); 4.40 and 4.50 (*AB*-system, $J_{AB} = 2$, 2H, =CH₂); 4.95 (s, 2H, CH₂); 7.10 and 8.40 (A_2X_2 -system, $J_{AX} = 8$, 4H, aromat. H). ¹³C-NMR ((D₆)DMSO): 24.6 (t, CH₂CH₂); 48.3 (t, CH₂NCH₂); 55.3 (q, OCH₃); 58.7 (t, CH₂); 86.5 (t, =CH₂); 108.1 (d, pyridinium β-C); 141.9 (d, pyridinium α-C); 153.1 (s, =COCH₃); 156.8 (s, pyridinium γ-C). Anal. calc. for C₁₃H₁₉ClN₂O₅ (328.5): C 48.99, H 6.00, N 8.79; found: C 49.34, H 6.23, N 8.74.

(E)-1-(2,3-Dibromo-1-propenyl)-4-(dimethylamino)pyridinium Perchlorate (10). A solution of Br₂ (0.9 g, 5.6 mmol) in CHCl₃ (5 ml) was added dropwise to a stirred suspension of $5a \cdot ClO_4^-$ (1.3 g, 5 mmol) in CHCl₃ (20 ml) at r.t. The suspension was stirred until a pale yellow solution was formed. The solvent was evaporated and the remaining crystalline residue heated under reflux in EtOH (10 ml) for 30 min. Removal of the solvent and recrystallization (EtOH) furnished pure 10 · perchlorate (2.0 g, 95%) as white needles, m.p. 152–154°. ¹H-NMR (CDCl₃/CF₃COOH): 3.43 (s, 6H, N(CH₃)₂); 4.24 (s, 2H, CH₂); 7.36 (s, 1H, =CH); 7.10 and 8.05 (A_2X_2 -system, $J_{AX} = 8$, 4H, aromat. H). ¹³C-NMR ((D₆)DMSO): 23.4 (t, CH₂); 40.1 (q, N(CH₃)₂); 100.5 (d, pyridinium β -C); 116.2 (s, BrC=); 124.4 (d, NCH=); 132.4 (d, pyridinium α -C); 147.1 (s, pyridinium γ -C). Anal. calc. for C₁₀H₁₃Br₂ClN₂O₄ (420.4): C 28.56, H 3.12, N 6.66; found: C 28.78, H 3.17, N 6.62.

1-(2,3-Dibromo-2-propenyl)-4-(dimethylamino)pyridinium Perchlorate (11a). A solution of Br₂ (1.08 g, 6 mmol) in CHCl₃ (5 ml) was added to a suspension of **3a** (1.3 g, 5 mmol) in CHCl₃ (25 ml) at r.t. A clear solution was formed. Stirring was continued for 30 min. The solvent was evaporated and the crystalline residue refluxed in EtOH (30 ml) for 1 h. Removal of the solvent gave **11a** · bromide, which was recrystallized from EtOH (1.9 g, 90%), as white needles, m.p. 139–141°. ¹H-NMR (CDCl₃/CF₃COOH): 3.26 (*s*, 6H, N(CH₃)₂); 5.14 (*s*, 2H, CH₂); 6.94 (*s*, 1H, CHBr); 6.89 and 7.88 (A_2X_2 -system, $J_{AX} = 8$, 4H, aromat. H). ¹³C-NMR (CDCl₃/CF₃COOH): 39.7 (*q*, N(CH₃)₂); 60.7 (*t*, CH₂); 108.2 (*d*, pyridinium β -C); 110.7 (*d*, =CHBr); 116.8 (*s*, =CBr); 141.5 (*d*, pyridinium α -C); 157.1 (*s*, pyridinium γ -C). Anal. calc. for C₁₀H₁₃Br₃N₂ (400.9): C 29.95, H 3.27, N 6.99; found: C 29.96, H 3.24, N 6.85.

REFERENCES

- a) A. R. Katritzky, O. Rubio-Teresa & R. C. Patel, Chem. Scr. 20, 147 (1982); b) A. R. Katritzky & O. Rubio, J. Org. Chem. 48, 4017 (1983); c) A. R. Katritzky & O. Rubio, J. Org. Chem., in press; d) A. R. Katritzky & M.J. Mokrosz, Heterocycles 22, 505 (1984).
- [2] M&T Chemicals Inc., Neth. Appl., 6,510,203 (Feb. 7, 1966); Chem. Abstr. 65, 2235d (1966).
- [3] V.A. Kabanov, K.V. Aliev & J. Richmond, J. Appl. Polym. Sci. 19, 1275 (1975); Chem. Abstr. 83, 79892n (1975).
- [4] V.A. Kargin, V.A. Kabanov, K. V. Aliev & R. Salimov, Ger. Offen. 1,954,255 (Jan. 14, 1971); Chem. Abstr. 74, 88376p (1971).
- [5] A. Mahamoud, J. P. Galy & E.J. Vincent, Synthesis 1981, 917.
- [6] J.-L. Dumont, W. Chodkiewicz & P. Cadiot, Bull. Soc. Chim. Fr. 1967, 1197.
- [7] B. Lupo & G. Tarrago, Synth. Commun. 12, 381 (1982).
- [8] I.I. Popov, P.V. Tkachenko & A.M. Simonov, Khim. Geterotsikl. Soedin. 1973, 551; Chem. Abstr. 79, 31984j (1973); I.I. Popov, P.V. Tkachenko & A.M. Simonov, ibid. 1975, 396; Chem. Abstr. 83, 28154r (1975).
- [9] I.N. Duling & C.C. Price, J. Am. Chem. Soc. 84, 578 (1962).
- [10] Unpublished work in this laboratory.