N-AMINOARYLPYRIDINIUM PERCHLORATES AND THEIR BEHAVIOR IN DIAZOTIZATION

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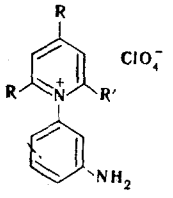
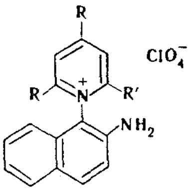
N-Aminoarylpyridinium salts react with nitrosyl perchlorate to give diazonium dications, which undergo diazo coupling, exchange a diazo group, and are cyclized by the Pschorr method.

It has been shown [1] that a convenient method for the synthesis of N-arylpyridinium salts is reaction of pyrylium salts with arylamines. N-Aminoarylpyridinium salts I and II, which we used in subsequent syntheses, are readily formed when various arylenediamines are introduced into this sort of reaction.*

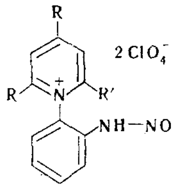


I

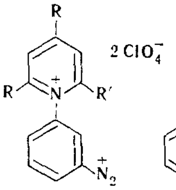


II

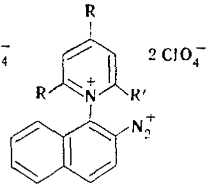
Thus diazonium dications IV and V, which are stable in solution and can be isolated in the crystalline state, are formed readily by the action of nitrosyl perchlorate in acetic acid on amines I and II. The reaction proceeds through the intermediate formation of nitrosamines (III), some of which (R = R' = CH_3, C_6H_5) were isolated in the individual state. When nitrosamines III are heated slightly in a mixture of glacial acetic acid and perchloric acid, they are converted to diazo compounds.



III



IV



V

The stability of the diazonium salts obtained above is explained by the peculiarity of the structure of N-arylpyridinium salts. Thus crystallographic investigations of N-

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*The structure of salts II was established by elimination of the amino group and comparison of the compounds obtained with authentically prepared N-(1'-naphthyl)pyridinium perchlorates.

Rostov State University. Scientific-Research Institute of Physical and Organic Chemistry, Rostov-on-Don. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1344-1348, October, 1974. Original article submitted June 26, 1972; revision submitted April 9, 1974.

TABLE 1. N-Arylpyridinium Perchlorates

Compound	R	R′	Substituent in the N-aryl ring	mp, °C	Empirical Formula	Found, %			Calc., %			Yield, %
						C	H	Halogen	C	H	Halogen	
I	CH_3	CH_3	2′-NH_2	157[a]	$C_{14}H_{17}ClN_2O_4$	53,5	5,3	11,7	53,7	5,4	11,3	79
	C_6H_5	C_6H_5	2′-NH_2	254—255[b]	$C_{29}H_{23}ClN_2O_4$	69,9	4,2	7,2	69,8	4,6	7,1	86
	C_6H_5	CH_3	2′-NH_2	242—243[c]	$C_{24}H_{21}ClN_2O_4$	65,6	4,9	7,9	65,9	4,8	8,1	85
	CH_3	CH_3	3′-NH_2	154—155[a]	$C_{14}H_{17}ClN_2O_4$	53,4	5,2	11,6	53,7	5,4	11,3	79
	C_6H_5	C_6H_5	3′-NH_2	269—270 (разл.)[c]	$C_{29}H_{23}ClN_2O_4$	70,0	4,6	7,4	69,8	4,6	7,1	92
	C_6H_5	C_6H_5	4′-NH_2	267—268 (разл.)[c]	$C_{29}H_{23}ClN_2O_4$	69,4	5,0	6,9	69,8	4,6	7,1	98
	CH_3	CH_3	4′-NH_2	176—177								
II	C_6H_5	C_6H_5	2′-NH_2	259—260[b]	$C_{33}H_{25}ClN_2O_4$	71,9	4,8	6,1	72,1	4,5	6,5	83
	C_6H_5	CH_3	2′-NH_2	213—214[b]	$C_{28}H_{23}ClN_2O_4$	68,8	4,8	7,6	69,0	4,7	7,2	78
	C_6H_5	C_6H_5	2′-H	273—274[c]	$C_{33}H_{24}ClNO_4$	73,9	4,2	6,3	74,2	4,5	6,6	86
	C_6H_5	CH_3	2′-H	225—226[d]	$C_{28}H_{22}ClNO_4$	71,0	4,7	7,8	71,2	4,7	7,4	85
VI	CH_3	CH_3	2′-H	128—129[1]								
	CH_3	CH_3	2′-Br	179—180[a]	$C_{14}H_{15}BrClNO_4$	45,0	4,1	30,2	44,6	4,0	30,6	66
	C_6H_5	C_6H_5	2′-H	264—265[7]								
	C_6H_5	C_6H_5	2′-Br	267—268[d]	$C_{29}H_{21}BrClNO_4$	61,5	3,3	20,3	61,8	3,7	20,5	70

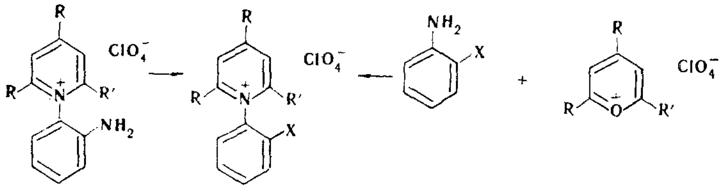
a) From water. b) From ethanol. c) From methanol. d) From glacial acetic acid.

TABLE 2. Characteristic Frequencies of the Bands of the Diazo Group in the IR Spectra of IV and V

Compound	R	R′	Position of the $-\overset{+}{N}\equiv N$ group	$\nu\ \overset{+}{N}\equiv N$, cm^{-1}
IV	CH_3	CH_3	2′	2270
	C_6H_5	C_6H_5	2′	2270
	C_6H_5	CH_3	2′	2290
	CH_3	CH_3	3′	2293
	C_6H_5	C_6H_5	3′	2285
	CH_3	CH_3	4′	2293
	C_6H_5	C_6H_5	4′	2290
V	C_6H_5	C_6H_5	2′	2285
	C_6H_5	CH_3	2′	2285

phenyl-2,4,6-trimethylpyridinium perchlorate [2] showed that the planes of the phenyl and pyridinium rings are at an angle of 83.5° with respect to one another. The C—N bridge bond does not have multiple character but rather is a simple σ bond. The data obtained by Camerman and co-workers [2] indicates the absence of interaction between the π electrons and the two rings, while the aryl substituent is subject only to the inductive effect of the pyridinium ring. The IR spectra of IV and V at 1570 and 1640 cm^{-1} contain absorption bands that are related to the vibrations of the pyridinium ring [1]. The broad intense band at 1070-1120 cm^{-1} is due to the presence of two ClO_4^- anions. The frequencies of the bands of the diazo group are presented in Table 2.

Because of the noncoplanarity of the pyridinium and phenyl rings in diazo compounds VI and V, the latter have all of the properties of arenediazonium salts. Thus the diazo group in IV (R = R′ = CH_3, C_6H_5) is exchanged by hydrogen and bromine via the Sandmeyer reaction. The structure of the products obtained was proved by alternative synthesis via the following scheme:



VI

VI X = H, Br

Dications IV and V undergo diazo coupling with N,N-dimethylaniline in glacial acetic acid to give N-arylazoarylenepyridinium salts VII and VIII.

The structure of the azo compounds obtained was proved by alternative synthesis from p-nitroso-N,N-dimethylaniline and the corresponding N-aminoarylpyridinium salts.

The presence of an o-diazo group in IV and V made it possible to accomplish the Pschorr synthesis. Derivatives of quinolizinium salts IX and X were obtained.

The UV spectra of IX and X contained the absorption bands characteristic for the quinolizinium cation [3].

EXPERIMENTAL

The IR spectra of mineral-oil suspensions of the compounds were recorded with a UR-20 spectrometer. The UV spectra of methanol solutions (c 10^{-5} M) were measured with a Specord UV-vis spectrophotometer.

N-Aminoarylpyridinium Perchlorates (I, II). A mixture of 10 mmole of the pyrilium salt [4], 10 mmole of arylenediamine, and 30 ml of ethanol was heated for 2 h. The resulting precipitate was removed by filtration. Data on the properties of the compounds obtained are presented in Table 1.

N-(2'-Nitrosamino)phenyl-2,4,6-triphenylpyridinium Perchlorate (III). A 0.33-g (2.5 mmole) sample of nitrosyl perchlorate [5] was added to a solution of 1.25 g (2.5 mmole) of N-(2-aminophenyl)-2,4,6-triphenylpyridinium perchlorate in 30 ml of glacial acetic acid, after which the mixture was stirred at 20° for 10-15 min. The yellow precipitate was removed by filtration and crystallized from ethanol to give 1.25 g (95%) of a product with mp 155-156° (dec.). Found: C 66.1; H 4.3; Cl 6.6%. $C_{29}H_{22}ClN_3O_5$. Calculated: C 65.9; H 4.2; Cl 6.7%.

N-(2'-Nitrosamino)phenyl-2,4,6-trimethylpyridinium Perchlorate. This compound was obtained by the method described above and was a hygroscopic yellow oil that exploded on heating.

N-Diazoarylpyridinium Diperchlorate (IV, V). A 1-ml sample of 70% perchloric acid and 5 mmole of nitrosyl perchlorate were added at room temperature to a solution of 5 mmole of N-aminoarylpyridinium perchlorate in 30 ml of glacial acetic acid, after which the mixture was stirred for 3-5 min. The crystalline precipitate of diazonium salt, which formed from the solution or was deposited when absolute ether was added, was removed by filtration and washed with ether. Crystalline diazo compounds IV and V exploded sharply on heating.

N-(p-N,N-Dimethylaminophenylazo)arylpyridinium Perchlorates (VII, VIII). A 5-mmole sample of N,N-dimethylaniline was added to a solution of a diazonium salt obtained from 5 mmole of N-aminoarylpyridinium salt in 30 ml of glacial acetic acid, after which the mixture was stirred at room temperature for 30 min. It was then diluted with water (100 ml), and the azo compound was extracted with chloroform. The solvent was removed by distillation. The residue was obtained as orange prisms (Table 3).

B) A mixture of 2 mmole of N-aminoarylpyridinium salt and 2 mmole of p-nitroso-N,N-dimethylaniline was heated in 10 ml of acetic anhydride for 2 h. The mixture was then cooled, and 0.5 ml of 70% perchloric acid and 50 ml of water were added to it. The precipitated azo compound was removed by filtration or extracted with chloroform.

The products obtained by this method were identical to the compound synthesized by method A.

Exchange of the Diazo Group in N-Diazoarylpyridinium Salts (IV) (R = C_6H_5; R' = CH_3). The diazo group in IV was replaced by hydrogen and bromine by the method in [6]. Data on the synthesized compounds (VI) are presented in Table 1.

Quinolizinium Perchlorates (IX, X). A diazonium salt obtained from 5 mmole of N-aminoarylpyridinium salt was added to 50 ml of absolute acetone. Nitrogen evolution was observed after the addition of copper powder to the solution. The solution was allowed to stand for 10 h, after which the solvent was removed by distillation. This method was used to obtain the compounds listed below.

6,8-Diphenyldibenzo[*a*, c]quinolizinium Perchlorate. This compound was obtained in 45% yield as yellow prisms with mp 305° (decomp., from glacial acetic acid). Found: C 72.4; H 4.4; Cl 7.1%. $C_{29}H_{20}ClNO_4$. Calculated: C 72.2; H 4.1; Cl 7.3%. UV spectrum, λ_{max}, nm (log ε): 227 (4.38), 243 (4.36), 278 (4.31), 303 (4.39), and 351 (4.08).

6-Methyl-8-phenyldibenzo[*a*, c]quinolizinium Perchlorate. This compound was obtained in 40% yield as yellow prisms with mp 212° (from ethanol). Found: C 68.3; H 3.9; Cl 8.2%. $C_{24}H_{18}ClNO_4$. Calculated: C 68.7; H 4.3; Cl 8.4%. UV spectrum, λ_{max}, nm (log ε): 224 (4.09), 259 (4.36), 272 (4.39), 326 (4.28), and 350 (4.02).

6,8-Diphenylbenzo[c]naphtho[1,2-*a*]quinolizinium Perchlorate. This compound was obtained in 50% yield as orange prisms with mp 256-257° (from ethanol). Found: C 74.7; H 4.3; Cl 6.7%. $C_{33}H_{22}ClNO_4$. Calculated: C 74.4; H 4.1; Cl 6.6%. UV spectrum, λ_{max}, nm (log ε): 222 (4.56), 225 (4.57), 242 (4.45), 247 (4.50), and 297 (4.45).

6-Methyl-8-phenylbenzo[c]naphtho[1, 2-*a*]quinolizinium Perchlorate. This compound was obtained in 40% yield as yellow prisms with mp 320° (from dimethylformamide). Found: C 71.2; H 4.3; Cl 7.9%. $C_{28}H_{20}ClNO_4$. Calculated: C 71.5; H 4.2; Cl 7.6%. UV spectrum, λ_{max}, nm (log ε); 221 (4.32), 223 (4.33), 242 (4.27), 271 (4.23), and 315 (4.47).

TABLE 3. N-(p-N,N-Dimethylaminophenylazo)arylenepyridinium Perchlorate

Compound	R	R'	Position of the azo group	mp, °C	Empirical formula	Found, %				Calc., %				λ_{max}, nm (lg ε)	Yield, %
						C	H	Cl	N	C	H	Cl	N		
VII	CH_3	CH_3	2'	200—201[a]	$C_{22}H_{25}ClN_4O_4$	59,1	5,6	8,1	12,7	59,3	5,6	7,9	12,6	312, 474 (4,68; 4,48)	96
	C_6H_5	C_6H_5	2'	192—193[b]	$C_{37}H_{31}ClN_4O_4$	70,1	4,7	5,3	8,4	70,4	4,9	5,6	8,8	314, 492 (4,69; 4,46)	56
	C_6H_5	CH_3	2'	212—212,5[b]	$C_{32}H_{29}ClN_4O_4$	67,5	5,3	6,4	9,6	67,5	5,1	6,2	9,8	304, 488 (4,07; 4,45)	68
	CH_3	CH_3	3'	206—207[c]	$C_{22}H_{25}ClN_4O_4$	59,0	5,9	8,0	12,9	59,3	5,6	7,9	12,6	243, 443 (4,35; 4,42)	50
	C_6H_5	C_6H_5	3'	253—254[c]	$C_{37}H_{31}ClN_4O_4$	70,1	5,1	5,3	9,1	70,4	4,9	5,6	8,8	312, 444 (4,49; 4,30)	77
	CH_3	CH_3	4'	217—218[b]	$C_{22}H_{25}ClN_4O_4$	59,4	6,0	7,6	12,5	59,3	5,6	7,9	12,6	278, 445 (4,87; 4,49)	77
	C_6H_5	C_6H_5	4'	204—205[c]	$C_{37}H_{31}ClN_4O_4$	70,1	5,1	5,4	8.4	70,4	4,9	5,6	8,8	313, 458 (4,91; 4,40)	75
VIII	C_6H_5	C_6H_5	2'	277—278[c]	$C_{41}H_{33}ClN_4O_4$	72,3	4,4	5,4	8,6	72,2	4,8	5,2	8,2	317, 427 (4,50; 4,21)	89
	C_6H_5	CH_3	2'	224—225[b]	$C_{36}H_{31}ClN_4O_4$	70,1	5,3	6,0	9,2	69,8	5,1	5,7	9,0	309, 493 (4,90; 4,18)	90

a) From water. b) From ethanol. c) From methanol.

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