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RESEARCHES ON SYNTHETIC DYES
LIV. Synthesis of Isomeric 1-Aryllepidine Salts and Use of IR Spectra to Determine Their Structures*

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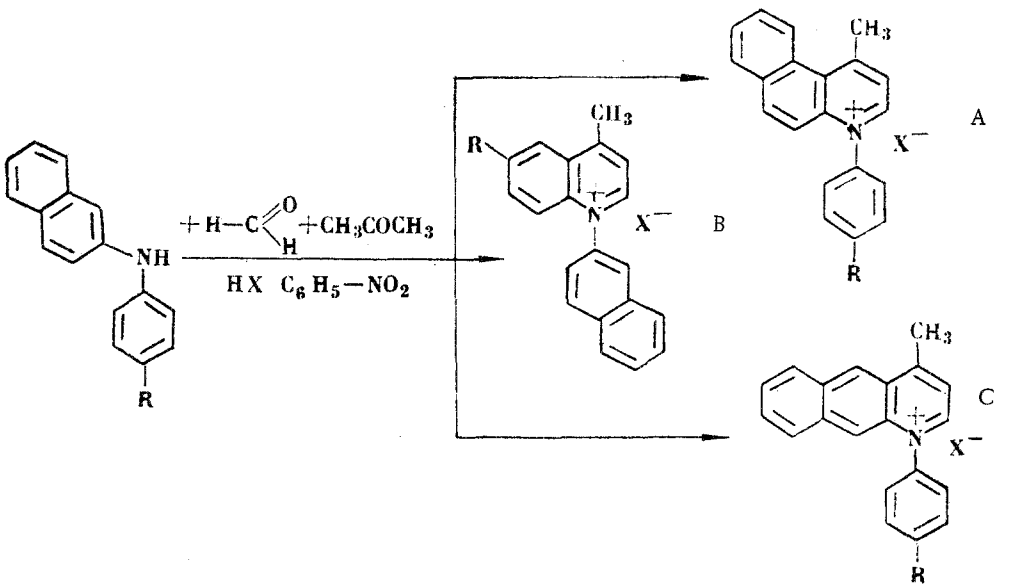
Reaction of phenyl-β-naphthylamines with formaldehyde and acetone in the presence of HCl and nitrobenzene in butanol solution leads to cyclization involving the naphthalene and phenyl rings, and formation of N-aryllepidine salts. 15 lepidine and 5, 6-benzoepidine salts are synthesized and characterized by their UV absorption spectra, as well as by their picrates.

It has previously been shown [1] that secondary aliphatic-aromatic and aromatic amines undergo the Baeyer reaction to give quaternary 1-alkyl- and 1-aryllepidine salts. The phenyl-substituted analogs have also been synthesized [2, 3].

In continuation of previous work, it was of interest to make use of cyclizations of phenyl-β-naphthylamine in the reaction when three isomeric quaternary salts A, B, and C can be formed:



Unlike syntheses of the corresponding quinaldine salts [4-7] Baeyer reaction cyclization conditions for all amines, except p-nitrophenyl-β-naphthylamine, result in formation of two isomeric salts A and B (Table 1). If the reaction is run in dry toluene or xylene A compounds only are found to be formed, and in lower yields than if it is run in butanol. The improbable isomer C could not be isolated in a single case under the reaction conditions studied. Isomer formation is influenced by the 5, 6-benzo group, which causes steric hindrance at the CH_3 group at position 4 in the quinoline ring, and thus to some extent favors formation of isomer B, where such steric hindrance is absent (Figs. 1 and 2).**

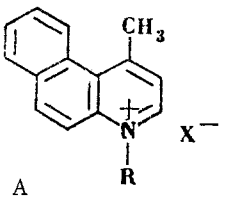
It is important to note that there are difficulties about separating the isomeric compounds (IIA-VIIA, and IIB-VIIB) formed. Thus, with the exception of IIIB, salts with the N-naphthyl structure are very readily soluble in water, and do not crystallize. Use of chromatography on Al_2O_3 results in the compounds synthesized undergoing a cyanine condensation. Complete purification of the N-β-naphthyl isomers was secured by evaporating the filtrates to dryness and then fractionally crystallizing from dry ethanol (VIB and VIIB), and water (IIIB), as well as by repeated precipitation from ethanol (IIB, IVB) and chloroform (VB) solutions with dry ether. 5, 6-benzo structure quinoline salts were recrystallized from ethanol (IIIA, VIIA, and IXA), from aqueous ethanol (IIA, VIA, VIIIA), and from water (IA, IVA), and they were also precipitated from chloroform solution (VA) with ether. The compounds prepared were also characterized as their picrates (Table 2).

*For Part LIII see [3].

**Regarding the atomic radii assumed in the diagrams, see [8, 9].

Table 1

1-Alkyl(aryl)-5,6-benzolepidinium (A) and 1-β-Naphthyl-6-substituted Lepidinium (B) Perchlorates



A

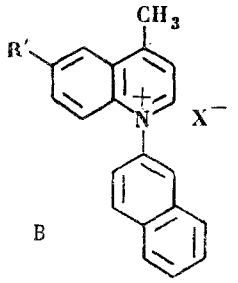
Compound No.		R	R'	X	Reaction time, hr	Mp, °C		λmax, mμ		lg ε		Formula
A	B					A	B	A	B	A	B	
I	—	CH_3	—	ClO_4	10	205–207		235 275 376	—	4.62 4.17 3.90	—	$C_{15}H_{14}ClNO_4$
II	II	C_6H_5	H	ClO_4	10	125–127	118–120	227 281 372	228 313	4.60 4.18 3.89	4.49 3.99	$C_{20}H_{16}ClNO_4$
III	III	p-$CH_3C_6H_4$	CH_3	ClO_4	7	244–245	158–159	232 279 372	228 318	4.62 4.15 3.92	4.51 4.00	$C_{21}H_{18}ClNO_4$
IV	IV	p-HOC_6H_4	OH	I	60*	196–198	246–248	223 285 375	232 332	4.65 4.19 3.93	4.51 4.02	$C_{20}H_{16}INO$
V	V	p-$CH_3COOC_6H_4$	CH_3COO	I	0,6	161–163	207–209	227 286 377	234 339	4.64 4.17 3.89	4.54 4.04	$C_{22}H_{18}INO_2$
VI	VI	p-$CH_3OC_6H_4$	CH_3O	ClO_4	5	154–156	127–129	225 261 360	227 315	4.65 4.21 3.87	4.56 4.01	$C_{21}H_{18}ClNO_5$
VII	VII	p-ClC_6H_4	Cl	ClO_4	7	168–170	232–234	224 275 373	227 325	4.63 4.18 3.88	4.58 4.07	$C_{20}H_{15}Cl_2NO_4$
VIII	—	p-$O_2NC_6H_4$	—	I	8	166–167	—	223 282 375	—	4.64 4.19 3.88	—	$C_{20}H_{15}IN_2O_2$
IX	—	β-$C_{10}H_7$	—	ClO_4	7	178–180	—	224 280 375	—	4.67 4.21 3.92	—	$C_{24}H_{18}ClNO_4$
X	X	p-—OC_6H_4	O—	—	—	—	—	238 301 438	250 420	4.65 4.16 3.86	4.57 4.04	

*Reaction run at 45°.

**Prepared by acetylating IVA and IVB.

***Isolated by means of $K_4[Fe(CN)_6]$

Table 1 (Continued)



Found, %								Calculated, %				Yield, %	
C		H		Halogen		N		C	H	Halogen	N	A	B
A	B	A	B	A	B	A	B						
58.26 58.37	—	4.63 5.50	—	11.45 11.57	—	4.50 4.59	—	58.34	4.58	11.52	4.55	38	—
64.88 65.03	65.00 64.87	4.40 4.30	4.42 4.32	9.64 9.68	9.52 9.58	3.75 3.86	3.84 3.72	64.95	4.36	9.59	3.79	20	5
65.80 65.66	65.73 65.75	4.65 4.68	4.80 4.77	9.19 9.29	9.31 9.21	3.61 3.70	3.58 3.60	65.71	4.73	9.24	3.65	31	9
58.18 58.08	58.06 58.16	3.84 3.92	3.97 3.85	30.63 30.68	30.77 30.74	3.47 3.33	3.31 3.44	58.12	3.90	30.71	3.39	34	12
57.94 58.05	58.10 57.97	5.04 5.06	4.93 5.01	27.95 27.97	27.81 27.83	3.01 3.15	3.14 3.02	58.03	4.98	27.88	3.08	87**	92**
62.99 63.01	63.15 63.04	4.50 4.58	4.60 4.48	8.81 8.96	8.84 8.80	3.56 3.45	3.53 3.43	63.08	4.54	8.87	3.50	36	15***
59.47 59.36	59.51 59.35	3.69 3.81	3.71 3.88	17.49 17.59	17.61 17.51	3.50 3.39	3.41 3.52	59.42	3.74	17.54	3.46	30	14
54.39 54.25	—	3.39 3.50	—	28.66 28.75	—	6.41 6.36	—	54.31	3.32	28.70	6.33	28	—
68.72 68.61	—	4.27 4.37	—	8.38 8.51	—	3.41 3.34	—	68.65	4.32	8.44	3.34	45	—
—	—	—	—	—	—	—	—	—	—	—	—	—	—

To confirm the structures of these isomers their UV spectra were determined and compared with those of salts prepared by cyclizing 1-methyl-β-naphthyl- and -β, β'-dinaphthylamines, where isomeric salts cannot be found (Table 1 and Fig. 3, 2, 4).

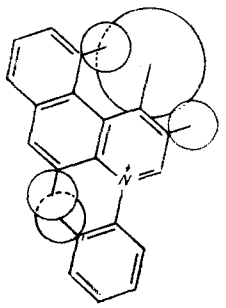


Fig. 1. Stereo formula for 1-phenyl-5,6-benzolepidine.

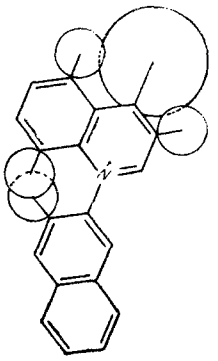


Fig. 2. Stereo formula for 1-β-naphthyllepidine.

The spectra of the quaternary salts with a 5, 6-benzo structure of the quinoline ring have three intense bands (Fig. 3, 2, 3, and 4) while salts which do not have that structure have two absorption maxima (Fig. 3, 1 and 5). A similar regularity is observed for the corresponding quinaldine compounds [10, 11].

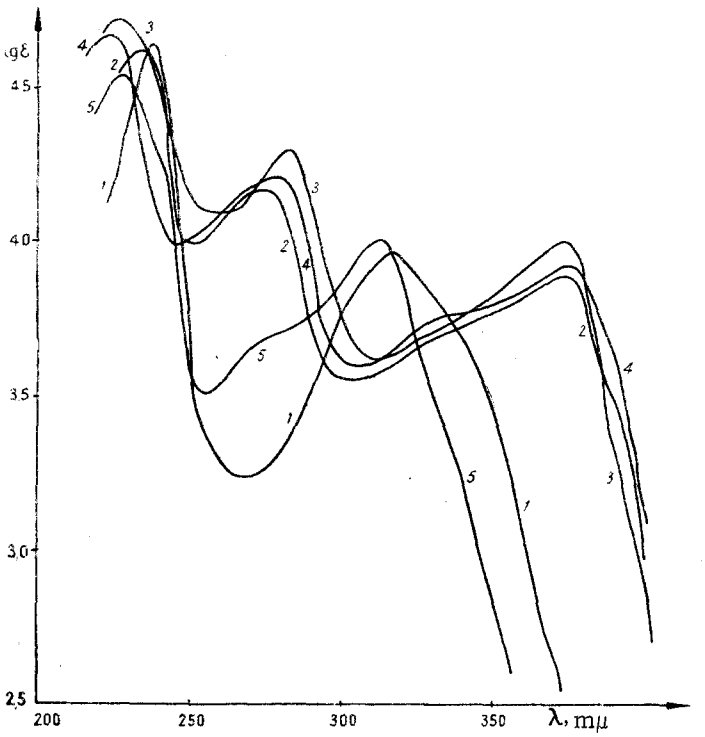


Fig. 3. UV absorption spectra of quaternary salts in ethanol: 1) 1-phenyllepidinium perchlorate; 2) 1-methyl-5,6-benzolepidinium perchlorate; 3) 1-phenyl-5,6-benzolepidinium perchlorate; 4) 1-β-naphthyl-5,6-benzolepidinium perchlorate; 5) 1-β-naphthyllepidinium perchlorate.

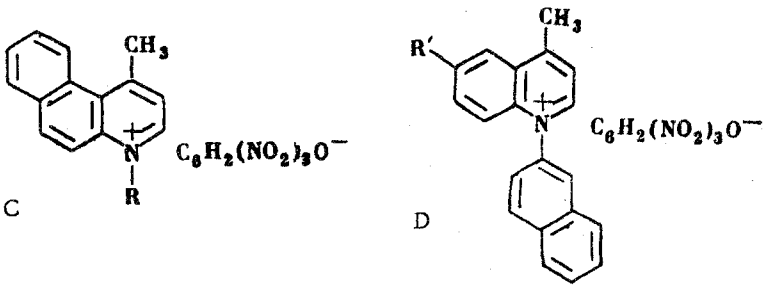
Comparison of the absorption maxima of 5, 6-benzolepidinium salts (Table 1A), shows that the long wave maximum is almost independent of the substituent at the p position in the phenyl ring (372-377 mμ). Compound VIA is an exception (λ_{max} 360 mμ) and this is connected with the effect of the methoxy group. With the short wave maxima the

deviation is more important (223-235 mμ). Comparison of the spectroscopic data for the compounds synthesized with the corresponding data for 5, 6-benzoquinaldinium salts [10, 11] shows increased coloration and lowering of absorption intensities. In the isomeric compound (B) the short wave maximum is inconsiderably changed by the presence of substituents at position 6 in the quinoline ring (6 mμ), while the long wave maximum suffers a considerable bathochromic shift (26 mμ). Change of the OH group to O^- (IVA and XA; IVB and XB) gives rise to a large bathochromic shift (15-88 mμ).

Experimental

1-Phenyl-5, 6-benzolepidinium perchlorate (IIA). A three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was charged with 5.5 g phenylnaphthylamine, 20 ml butanol, 2.6 ml nitrobenzene, 9.2 ml acetone, and 5 ml concentrated HCl, the mixture heated to 100°, and 2.5 ml 30% formaldehyde in 40 ml water added over 1 hr. Heating was continued for a further 10 hr, with constant stirring. The dark reaction products were steam distilled, filtered, boiled with active carbon, filtered, and to the filtrate an aqueous solution of $NaClO_4$ was added until no further precipitate was formed. The whole was left for 24 hr at room temperature, the precipitate filtered off, and recrystallized from water-ethanol until its melting point was constant. Finely divided, yellow crystalline powder, yield 1.8 g (20%), mp 125-127°. The salt was readily soluble in ethanol, acetone, chloroform, pyridine, and acetic anhydride, sparingly soluble in benzene and water, and practically insoluble in ether.

Table 2



1-Alkyl (aryl)-5, 6-benzolepidinium (C) and 1-β-Naphthyl-6-R'-lepidinium (D) Picrates

Compound No.		R	R'	Mp (decomp), °C		Formula	Found, N, %		Calculated, N, %	Yield, %	
C	D			C	D		C	D		C	D
I	—	CH_3	—	169–171	—	$C_{21}H_{16}N_4O_7$	12.92 12.85	—	12.84	82	—
II	II	C_6H_5	H	177–179	213–215	$C_{26}H_{18}N_4O_7$	11.30 11.27	11.20 11.18	11.24	85	90
III	III	p-$CH_3C_6H_4$	CH_3	164–166	227–229	$C_{27}H_{20}N_4O_7$	10.88 10.97	10.81 10.94	10.93	92	93
IV	IV	p-HOC_6H_4	OH	150–152	192–194	$C_{26}H_{18}N_4O_8$	10.97 10.86	10.85 10.97	10.89	87	93
V	V	p-$CH_3COOC_6H_4$	CH_3COO	148–150	217–219	$C_{28}H_{20}N_4O_9$	10.01 10.10	10.13 10.00	10.07	86	91
VI	VI	p-$CH_3OC_6H_4$	CH_3O	159–161	201–203	$C_{27}H_{20}N_4O_8$	10.65 10.63	10.67 10.53	10.60	90	92
VII	VII	p-ClC_6H_4	Cl	130–132	205–207	$C_{26}H_{17}ClN_4O_7$	10.46 10.58	10.61 10.58	10.51	92	94
VIII	—	p-$O_2NC_6H_4$	—	133–135	—	$C_{26}H_{17}N_5O_9$	12.92 12.85	—	12.89	82	—
IX	—	β-$C_{10}H_7$	—	193–195	—	$C_{30}H_{20}N_4O_7$	10.26 10.15	—	10.22	87	—

1-β-Naphthyllepidinium perchlorate (IIB). The filtrate obtained in the IIA experiment was evaporated to dryness. The dark gummy hygroscopic precipitate was dried in a vacuum desiccator, and then triturated a few times with small quantities of cold dry ethanol. As a result the precipitate became paler. It was dissolved in boiling dry ethanol, filtered, and dry ether added after cooling to 0°. On standing the salt separated as dark yellow flocs. It was purified by precipitation from dry ethanol with ether. Minute pale yellow plates, mp 118-120°, yield 0.45 g (5%). The salt is readily soluble in water. The quaternary salts IA, IIIA-IIIB, VIA-VIB, and VIIIA were prepared similarly. Compounds IVA-VIB, VIIA-VIIB, and IXA were synthesized in sealed tubes.

1-Phenyl-5,6-benzolepidinium picrate (IIC). An ethanol-water solution of 3.7 g 1-phenyl-5,6-benzolepidinium perchlorate was prepared and a saturated ethanol-water solution of picric acid added dropwise until no further turbidity appeared. After standing for 24 hr at room temperature, the precipitate was filtered off and recrystallized from ethanol. Finely divided, yellow crystalline powder, mp 177-179° (decomp). Yield 4.2 g (85%). The salt was readily soluble in acetone and pyridine, sparingly soluble in water, insoluble in ether. With the exception of salts containing acetoxy groups, the other picrates were prepared similarly.

Compounds VA-C. 0.005 mole of the appropriate hydroxyl-containing salt of IV and 6 ml acetic anhydride, were refluxed gently for 40 min. To purify the salt it was reprecipitated from chloroform with ether (VA, VB), or from acetone-chloroform mixture (VB, VC).

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