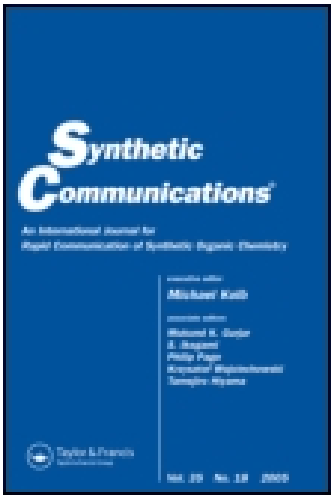

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Synthesis and Characterization of New Derivatives of 1,4-Diazepinium Salts

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SYNTHESIS AND CHARACTERIZATION OF NEW DERIVATIVES OF 1,4-DIAZEPINIUM SALTS

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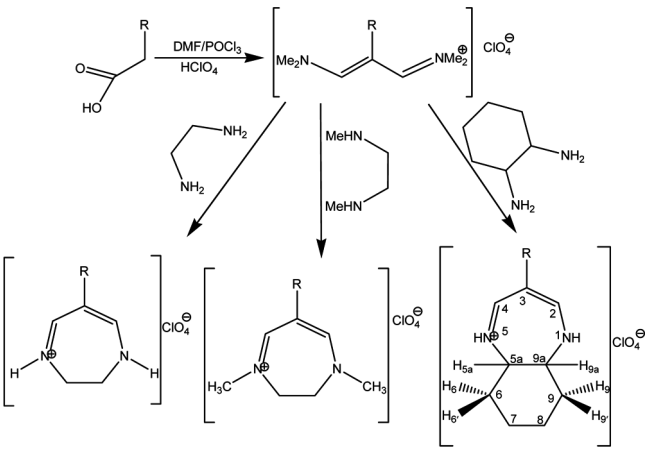
Persian Gulf University, Bushehr, Iran

GRAPHICAL ABSTRACT



Abstract *Novel 6-aryl-1,4-diazepinium and 3-aryl-hexahydro-1H-benzo-[b-1,4]-diazepinium salts (with aryl and heteroaryl = 1-quinilinio, 3,5-dimethylpyridinio, 4-phenyl phenyl, 3,4,5-trimethoxyphenyl, and 1,4-phenylene) were synthesized mostly by reactions of 1,2-diamines with 3-aryl and 3-heteroaryl-1,5-diazapentadienium salts. The ultraviolet spectral behavior of these compounds was examined in acetonitrile. Elemental analysis, infrared, ^{1}H NMR, ^{13}C NMR, and mass spectra confirmed the molecular structure of the newly synthesized compounds.*

Keywords 3-Aryl-hexahydro-1H-benzo-[b-1,4]-diazepinium salts; 3-arylvinamidinium salts; 6-aryl-2,3-dihydro-1,4-diazepinium salts; Vilsmeier reaction

INTRODUCTION

1,4-Diazepines have attracted attention as an important class of heterocyclic compounds in the field of drugs and pharmaceuticals.[1–6] Among these compounds, 1,4-benzodiazepines such as diazepam, oxazepam, nordiazepam, and lorazepam are

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successfully used as drugs for the treatment of anxiety, sleep disturbance, and status epilepticus. 1,4-Diazepines also show biological activities such as anticancer, antibacterial, and antiviral activities.[7–9] Because of their broad spectrum of biological activity, these compounds have received a great deal of attention in connection with their synthesis.

Although many different 1,4-diazepinium derivatives have been synthesized,[10] to the best of our knowledge, very little attention has been paid to the synthesis of 6-aryl and 6-heteroaryl-1,4-diazepinium salts.[11]

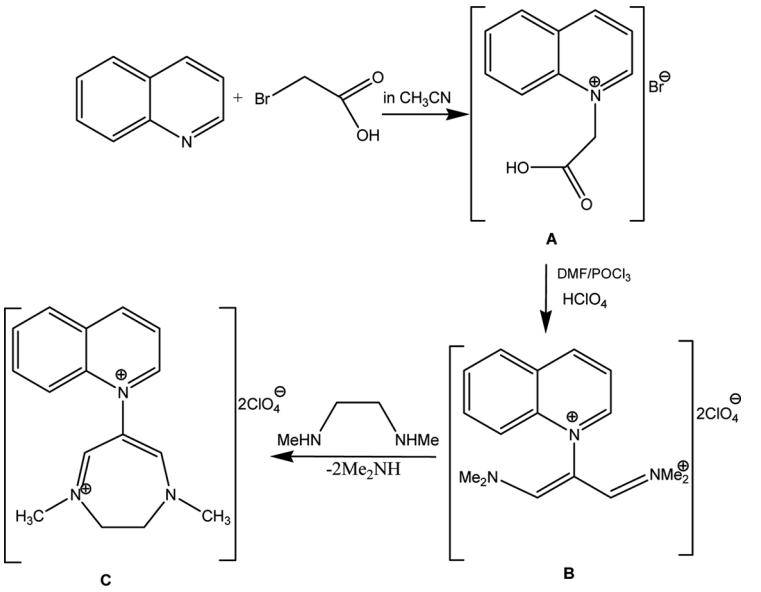
In this article, we describe the synthesis of a variety of 6-aryl and 6-heteroaryl-2,3-dihydro-1,4-diazepinium and 3-aryl-hexahydro-1H-benzo-[b-1,4]-diazepinium salts and evaluate their structural properties on the basis of their ultraviolet (UV) absorption, infrared (IR), ^{1}H NMR, ^{13}C NMR, and mass spectra.

RESULTS AND DISCUSSION

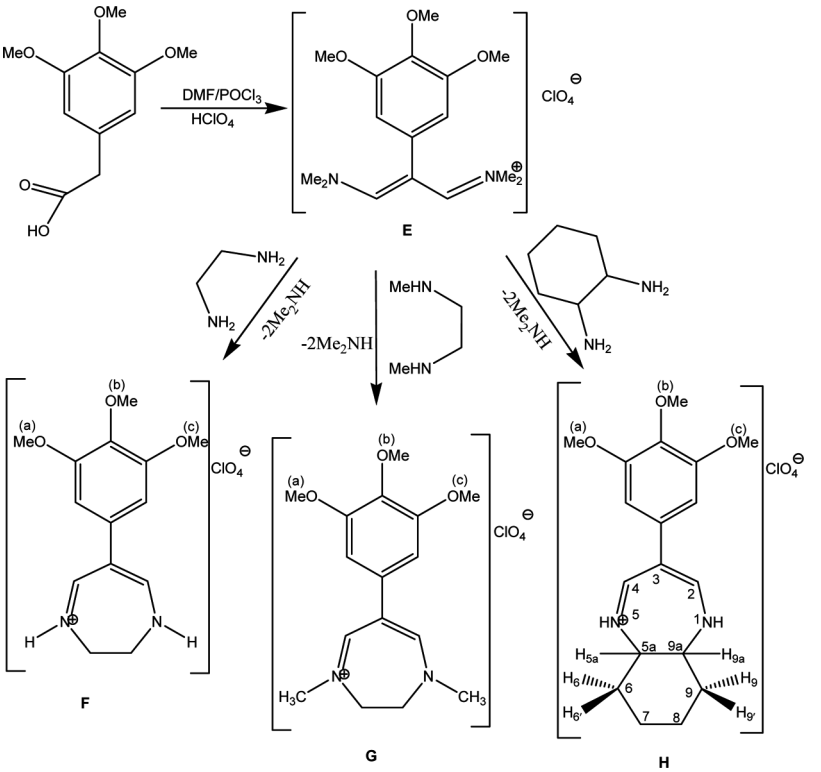
A variety of 6-aryl-2,3-dihydro-1,4-diazepinium and 3-aryl-hexahydro-1H-benzo-[b-1,4]-diazepinium salts (with aryl and heteroaryl = 1-quinilinio, 3,5-dimethylpyridinio, 4-phenyl, 3,4,5-trimethoxyphenyl, and 1,4-phenylene) were obtained, for the most part in good yields (see Table 1). The most used method of preparation, exemplified in Schemes 1, 2, and 3, starts from an arylacetic acid, which is first converted into a 3-arylvinamidinium salt by means of Vilsmeier–Arnold

Table 1. Empirical formula, elemental analyses, yields, melting points, and UV spectral data (measured in acetonitrile) of the 6-aryl-4-diazepinium salts C, D, F, G, H, I, and K and the intermediates A, B, E, and J

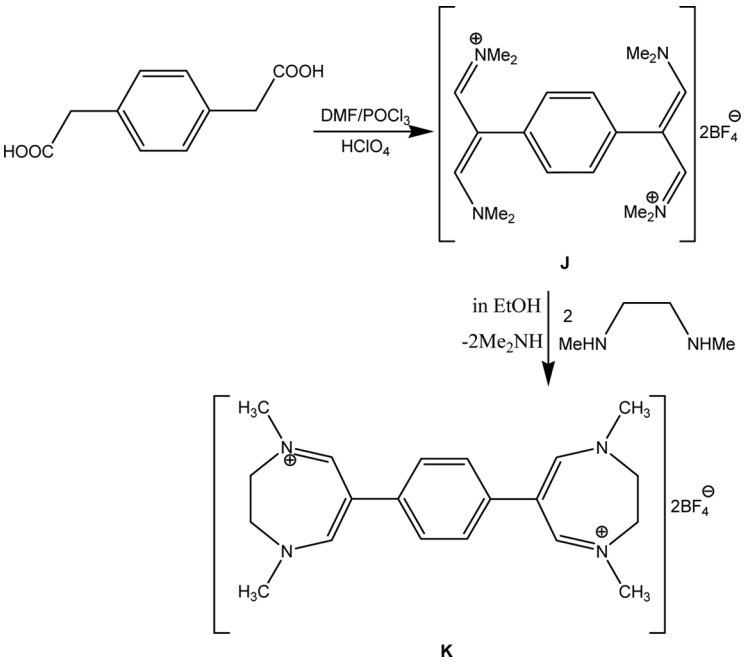
Compound	Empirical formula (mol. mass)	Calculated found (%) C	H	N	Yield (%)	Mp (°C)	λ_{max} (nm)	lg ε_{max} ($M^{-1}cm^{-1}$)
A	$(C_{11}H_{10}NO_2)Br$ (188.0)	49.29 (49.30)	3.76 (3.76)	5.23 (5.31)	56	229		
B	$(C_{16}H_{21}N_3)(ClO_4)_2$ (453.8)	42.38 (41.49)	4.63 (5.00)	9.27 (9.01)	80	269		
C	$(C_{16}H_{21}N_3)(ClO_4)$ (452.2)	42.49 (41.05)	4.23 (4.91)	9.29 (9.01)	63	258	337	4.42
D	$(C_{14}H_{21}N_3)(BF_4)_2$ (405.2)	41.52 (42.01)	5.23 (5.24)	10.38 (10.42)	80	245–247	340	4.26
E	$(C_{16}H_{25}N_2O_3)(ClO_4)$ (392.5)	48.92 (50.05)	6.37 (6.42)	7.13 (8.10)	64	178		
F	$(C_{14}H_{19}N_2O_3)(ClO_4)$ (362.0)	46.35 (47.01)	5.28 (6.03)	7.72 (8.20)	66	181–183	254, 360	4.02, 3.96
G	$(C_{16}H_{23}N_2O_3)(ClO_4)$ (390.8)	49.17 (51.05)	5.93 (6.42)	7.17 (8.10)	80	222	258, 373	4.09, 4.01
H	$(C_{18}H_{25}N_2O_3)(ClO_4)$ (416.9)	51.86 (51.78)	6.04 (6.33)	6.72 (6.53)	85	235	257, 361	4.20, 3.82
I	$(C_{21}H_{23}N_2)(ClO_4)$ (402.9)	63.38 (62.01)	6.04 (6.65)	6.95 (6.85)	78	313	275, 361	4.50, 3.93
J	$(C_{20}H_{32}N_4)(BF_4)_2$ (502.3)	47.84 (49.02)	6.42 (6.10)	11.16 (12.04)	66	280		
K	$(C_{20}H_{28}N_4)(BF_4)_2$ (498.2)	48.23 (49.01)	5.67 (5.25)	11.25 (12.21)	59	290	281, 371	4.47, 4.38



Scheme 1. Reaction pathway to diazepinium salt **C**.



Scheme 2. Reaction pathway to the diazepinium salts **F**, **G**, and **H**.



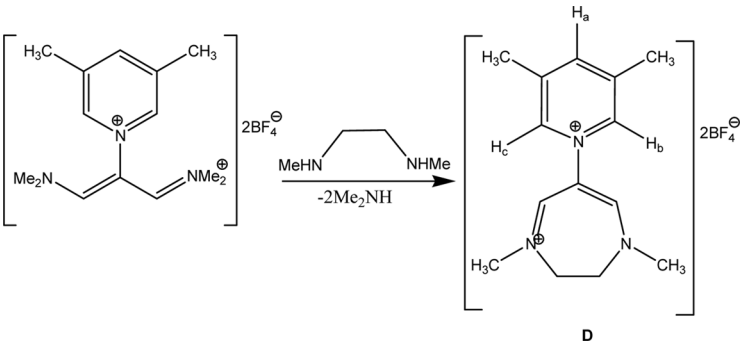
Scheme 3. Reaction pathway to diazepinium salt **K**.

formylation.[12,13] This salt in turn reacts with ethane-1,2-diamine, *N,N′*-dimethylethane-1,2-diamine, or cyclohexane-1,2-diamine to provide the corresponding diazepinium salts.

The new 6-heteroaryl-1,4-diazepinium salt **C** was synthesized using a three-step procedure as shown in Scheme 1: (i) synthesis of the *N*-heteroaryl acetic acid **A** using the reaction between quinoline with bromoacetic acid;[14] (ii) synthesis of 3-heteroarylvinamidinium salt **B** by Vilsmeier–Arnold formylation of A;[12,13] and (iii) synthesis of **C** from **B** with *N,N′*-dimethylethane-1,2-diamine. Scheme 4 shows the preparation of **D** from 1,1,5,5-tetramethyl-3-(3,5-dimethylpyridinium-1-yl)-1,5-diazapentadienium bis(tetrafluoroborate)[15] by reaction with *N,N′*-dimethylethane-1,2-diamine. The 1,4-diazepinium salts **F**, **G**, and **H** were synthesized from the 3,4,5-trimethoxyphenyl vinamidinium salt **E** by reaction with ethane-1,2-diamine, *N,N′*-Dimethylethane-1,2-diamine, and cyclohexane-1,2-diamine, respectively (Scheme 2). The preparation of the 1,4-diazepinium salts **I** and **K** are depicted in Schemes 5 and 3, respectively.

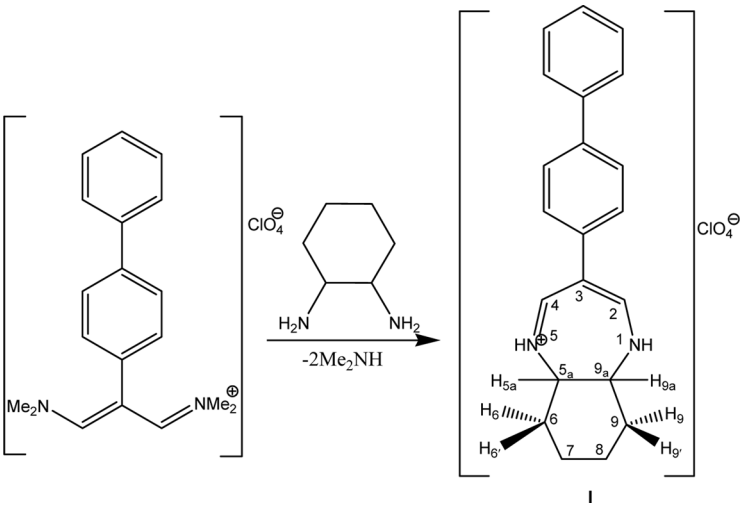
All diazepinium salts **C**, **D**, **F**, **G**, **H**, **I**, and **K** and the intermediates **A**, **B**, **E**, and **J** are new compounds, the molecular structures of which were confirmed by elemental analysis (Table 1), ^{1}H NMR, ^{13}C NMR, IR, and mass spectroscopy (Table 2). Inspection of the data presented in Table 1 shows that the melting points of all compounds are rather sharp, indicating the high purity of all synthesized compounds.

The ^{13}C NMR spectra of the 1,4-diazepinium salts, like the ^{1}H NMR spectra, confirm shape and charge distribution of these compounds. As for other diazepinium



Scheme 4. Reaction pathway to the diazepinium salt **D**.

salts,[11,16] the most striking feature of the ^{13}C NMR spectra of the 6-aryl derivatives is the large difference in chemical shift between the signals for C-6 ($\Delta\delta \approx .106$ ppm) and C-5,7 ($\Delta\delta \approx 157$ ppm), indicating the strongly alternating charge density in the conjugated vinamidinium chain, which is typical for such polymethine π-systems.[16] The influence of the 6-aryl substituents (**F**, **G**, **H**, **I**, and **K** salts) on the chemical shift of **C**-6 is very similar to that found for the *N*-aryl derivatives (**C** and **D** salts) (Table 2). The long-wavelength UV absorption data ($\lambda_{max} \approx 340$–$373$ and ε_{max} values) of the 1,4-diazepinium salts **C**, **D**, **F**, **G**, **H**, **I**, and **K**, measured in acetonitrile, are also depicted in Table 1. It is noteworthy that the C and D salts show only one peak and the **F**, **G**, **H**, **I**, and **K** salts show two peaks attributed to the $\pi \rightarrow \pi^*$ transitions of the salts.



Scheme 5. Reaction pathway to the diazepinium salt **I**.

Table 2. Spectral data of the 6-aryl-4-diazepinium salts C, D, F, G, H, I, and K and the intermediates A, B, E, and J

Compound	IR (cm^{-1})	^1H NMR (DMSO) δ/ppm (assignment)	^{13}C NMR (DMSO) δ/ppm (assignment)	Mass spectra
A	3500 (broad, COOH)	6.15 (s, 2H, CH_2) 8.03–8.56 and 9.43–9.46 (m, 7H quinoline) 9.73 (s, 1H, COOH)	57.7 (CH_2) 118.7, 121.9, 129.3, 129.8, 130.6, 135.9, 138.2, 148.6, 150.8, 167.2 (COOH)	188 [M^+-Br^-]
B	1530 (broad, s, C=N) 1089 (s, ClO_4^-)	1.97(wide, s, 6H, NMe_2)3.29(s, 6H, NMe_2^+) 8.15–8.37 and 9.57–9.59 (m, vinyl and quinoline)	37.2 (s, CMe_2) 49.7 (s, NCH_3) 102.6, 120.0, 122.3, 129.1, 131.1, 131.5, 138.1, 140.5, 152.1, 154.2, 158.8 (vinyl)	255 [M^+-2ClO_4^-]
C	1600 (s, C=N) 1090 (broad, ClO_4^-)	3.46 (s, 6H, Me_2N) 4.11 (wide, s, 4H, CH_2CH_2) 8.08–8.6 (m, 7H, quinoline) 9.49 (wide, s, 2H, N=CH, diazepine)	48.21 and 56.05 (CH_2CH_2 and NCH_3) 106.06 (N=CH-C)[C_6] 120.99, 122.77, 130.19, 130.82, 130.91, 136.74, 141.40, 149.79, 153.93, 157.33 (N=CH-C) [C_5 or C_7]	253 [M^+-2ClO_4^-]
D	1585 (s, C=N) 1052 (s, BF_4^-)	2.49 (s, 6H, Me-pyridine) 3.45 (s, 6H, NMe) 3.86 (s, 4H, CH_2CH_2) 8.35 (s, 2H, N=CH diazepin) 8.43 (s, 1H, H_a-pyridine) 8.32 (s, 2H,H_b and H_c-pyridine)	18.06 (Me-pyridine) 48.10 and 55.93 (CH_2CH_2 and NCH_3) 110.88 (N=CH-C) [C_6] 138.14 and 147 (C-pyridine) 156.55 (N=CH-C) [C_5 or C_7]	231 [M^+-2BF_4^-]
E	1580 (broad, s, C=N) 1000 (s, ClO_4^-)	2.59 (s, 6H, OCH_3 [a and b]) 3.36 (s, 3H, OCH_3) [*b*]) 3.87 (s, 6H, NMe_2) 3.88 (s, 6H, NMe_2^+) 6.48 (s, 2H, phenyl) 7.81 (s, 2H, vinyl, H-β)	39.30 (NMe_2) 49.14 (NMe_2^+) 56.43 and 61.17 (OCH_3) 105.66 (C-α) 109.44, 127.31, 138.37, 153.27, 163.83 (vinyl and phenyl)	293 [M^+-ClO_4^-]
F	1590 (broad, s, C=N) 1401 (s, C-O) 1085 (s, ClO_4^-)	3.64 (s, 3H, OCH_3 [b]) 3.70 (s, 4H, CH_2CH_2) 3.80 (s, 6H, OCH_3 [a and c]) 6.56 (s, 2H, phenyl) 7.99 (s, 2H, N=CH) 10.20 (s, 2H, NH)	49.28 (CH_2CH_2), 56.41, 60.43, 103.52, 105.70 (N=CH-C) [C_6] 135.16, 136.68, 153.32, 157.93 (N=CH-C)[C_5 or C_7]	263 [M^+-ClO_4^-]

G	1580 (broad, C=N) 1100 (broad, C=CH vinyl) 1080 (s, ClO_4^-)	3.47 (s, 6H, OCH_3 [a and c]) 3.63 (s, 4H, CH_2CH_2) 3.77 (s, 3H, OCH_3 [b]) 3.81 (s, 6H, NCH_3) 6.57 (s, 2H, phenyl) 7.96 (s, 2H, vinyl)	47.94 and 55.81 (CH_2CH_2 and NCH_3) 56.47, 60.52, 102.87, 106.06 (N=CH-C) [C_6] 135.41, 136.71, 153.23, 158.02 (N=CH-C) [C_5 or C_7]	291 [M^+-ClO_4^-]
H	1593 (broad, s, C=N) 1414 (s, C-O)1080 (s, ClO_4^-)	1.31–1.43 (m, 4H, CH_2CH_2) 1.75 (m, 2H, H_6 and H_9) 2.35–2.49 (m, 2H, H_6 and H_9) 3.27 (s, 2H, H_{5a} and H_{9a}) 3.63 (s, 3H, OCH_3 [b]) 3.80 (s, 6H, OCH_3 [a and c] 6.58 (s, 2H, phenyl) 7.77 (s, 2H, N=CH) 10.11 (s, 2H, NH)	23.08, 30.82, 56.44, 60.47, 60.67, 103.15, 105.59 (N=CH-C)[C_3] 134.60, 136.76, 153.38, 156.15 (N=CH-C) [C_2 or C_4]	317 [M^+-ClO_4^-]
I	1550 (broad, s, C=N) 1050 (s, ClO_4^-)	1.32–1.43 (m, 4H, CH_2CH_2) 1.75 (m, 2H, H_6 and H_9) 2.35–2.38 (m, 2H, H_6 and H_9) 3.21–3.23 (m, 2H, H_{5a} and H_{9a}) 7.36–7.83 (m, 11H, N=CH and biphenyl) 10.23 (s, 2H, NH)	23.09 (CH_2CH_2) 30.81, 60.71 (C_{5a} and C_{9a}) 102.34 (N=CH-C) [C_3] 126.93, 127.45, 127.91, 128.05, 129.48, 137.91, 138.47, 140.02, 156.00 (N=CH-C) [C_2 or C_4]	303 [M^+−ClO_4^-]
J	1520 (broad, s, C=N) 1053 (broad, s, BF_4^-)	2.44 (s, 12H, NMe_2) 3.23 (s, 12H, NMe_2^+) 7.38 (s, 4H, phenyl) 7.72 (s, 4H, vinyl)	49.09 (N-CH_3) 104.76 (C-3 and 3′) 132.69, 133.89, 163.47 (C-2 and 2′)	328[M^+-ClO_4^-]
K	1510(broad, s, C=N) 1051(broad, s, BF_4^-)	3.49 (s, 12H, NMe) 3.79 (s, 8H, CH_2CH_2) 7.34 (s, 4H, phenyl 7.98 (s, 4H, N=CH, diazepine)	48.01 and 55.91 (CH_2CH_2 and NMe) 101.86 (N=CH-C) [C_3] 128.03, 137.41, 157.85 (N=CH-C) [C_2 or C_4]	324[M^+-ClO_4^-]

CONCLUSION

Seven novel 6-aryl and 6-heteroaryl-1,4-diazepinum salts were synthesized, mostly by reactions of 1,2-diamines with 3-aryl-1,5-diazapentadienium salts, in good yields. The molecular structure and purity of the newly prepared compounds were confirmed by IR, NMR, mass spectroscopy, and elemental analyses.

EXPERIMENTAL

General Methods

All reactants and chemicals were purchased from Merck or prepared according to literature procedures. Solvents were of analytical grade.

^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance DRX-500. Dimethyl sulfoxide (DMSO) and deuterated chloroform ($CDCl_3$) were used as solvent and tetramethylsilane (TMS) as internal standard.

Mass spectral data were obtained on a Finnigan-Matt 8430 (70-eV) spectrometer.

UV absorption spectra were recorded at room temperature in acetonitrile using a Perkin-Elmer Lambda 25 spectrophotometer, and the IR spectra were obtained with a Perkin-Elmer 781 spectrophotometer.

Elemental analyses with KBr discs were made with a CHN Analyzer [Flash, 1112 series (EA), Thermo Finnigan Company], and the melting points were determined on the Electrothermal 9200 apparatus.

General Experimental Procedures

N-(Hydroxycarbonylmethyl)quinolinium bromide (A). Quinoline (10.0 g, 0.08 mol) was added to 11.0 g (0.08 mol) of bromoacetic acid in 40 mL of acetonitrile. The mixture was refluxed at 60 °C for 7 h. The brown crystals of **A** were collected by filtration, recrystallized from ethanol, and dried in a desiccator with P_4O_{10}.[14]

1,1,5,5-Tetramethyl-3-(1-quinolinio)-1,5-diazapentadienium bis(perchlorate) (B). Phosphorus oxitrichloride (8.19 mL, 0.09 mol) was added to 16.50 mL (0.21 mol) of DMF at 0 °C, and the mixture was stirred at room temperature for 30 min. *N*-(hydroxycarbonylmethyl)quinolinium bromide **A** (8.04 g 0.03 mol) was added to this reagent. The mixture was refluxed at 75–80 °C for 5 h and then set aside in a refrigerator for 12 h. The solution was then diluted with precooled and dried ethanol (100 mL).

A solution of 72% $HClO_4$ (10.00 mL, 0.10 mol) in ethanol (30 mL) was added to this solution, and the mixture was set aside in a refrigerator for 12 h. The yellow crystals of **B** were collected by filtration, washed with diethyl ether, and dried in a desiccator with P_4O_{10}.[12,13]

6-(1-Quinolinio)-2,3-dihydro-1,4-dimethyl-1H-1,4-diazepinium bis(perchlorate) (C). Solutions of 0.45 g (0.001 mol) of 1,1,5,5-tetramethyl-3-(1-quinolinio)-1,5-diazapentadienium bis(perchlorate) **B** in 20 mL of acetonitrile and 0.10 mL (0.001 mol) of *N,N′*-dimethylethane-1,2-diamine in 20 mL of acetonitrile were added simultaneously drop by drop to boiling acetonitrile (20 mL). The

resultant solution was refluxed at 85 °C for 8 h. After cooling to room temperature, the solvent was evaporated under vacuum, and the red precipitate formed was collected by filtration, recrystallized from dry ethanol, and dried in a desiccator with P_4O_{10}.

6-[1-(3,5-Dimethylpyridinio)]-2,3-dihydro-1,4-dimethyl-1H-1,4-diazepinium bis(tetrafluoroborate) (D). Solutions of 0.48 g (0.001 mol) of 1,1,5,5-tetramethyl-3-(3,5-dimethylpyridinium-1-yl)-1,5-diazapentadienium bis(tetrafluoroborate)[15] in 15 mL of acetonitrile and 0.10 mL (0.001 mol) of *N,N′*-dimethylethane-1,2-diamine in 15 mL of acetonitrile were added simultaneously drop by drop to boiling acetonitrile (15 mL). The reaction mixture was refluxed at 85 °C for 7 h. After cooling to room temperature, the solvent was evaporated under vacuum, and the resultant oily red residue was kept cold overnight. Then a small amount of dichloromethane was added, and the precipitate formed was collected by filtration, recrystallized from 2-propanol, and dried in a desiccator with P_4O_{10}.

1,1,5,5-Tetramethyl-3-[(3,4,5-trimethoxy)phenyl]-1,5-diazapentadienium perchlorate (E). Phosphorus oxitrichloride (1.80 mL, 0.02 mol) was added to 3.30 mL (0.04 mol) of DMF at 0 °C, and the mixture was stirred at room temperature for 30 min. 3,4,5-Trimethoxyphenyl acetic acid (purchased from Merck: 1.50 g; 0.006 mol) was added to this reagent. The mixture was refluxed at 80 °C for 7 h and then set aside in a refrigerator for 12 h. The solution was then diluted with precooled and dried ethanol (20 mL).

A solution of 72% $HClO_4$ (1.7 mL, 0.01 mol) in ethanol (10 mL) was added to this solution, and the mixture was set aside in a refrigerator for 12 h. The yellow crystals of salt **E** were collected by filtration, washed with diethyl ether, and dried in a desiccator with P_4O_{10}.[12,13]

6-(3,4,5-Trimethoxyphenyl)-2,3-dihydro-1,4-dihydro-1H-1,4-diazepinium perchlorate (F). Solutions of 0.39 g (0.001 mol) of 1,1,5,5-tetramethyl-3-(3,4,5-trimethoxyphenyl)-1,5-diazapentadienium perchlorate **E** in 15 mL of acetonitrile and 0.07 mL (0.001 mol) of ethane-1,2-diamine in 15 mL of acetonitrile were added simultaneously drop by drop to boiling acetonitrile (15 mL).[17] The resultant yellow solution was refluxed at 85 °C for 5 h. After evaporating the solvent under vacuum, an oily residue was obtained and mixed with 3 mL of dichloromethane. The resultant gray precipitate was collected by filtration, washed with diethyl ether, and dried in a desiccator with P_4O_{10}.

6-(3,4,5-Trimethoxyphenyl)-2,3-dihydro-1,4-dimethyl-1H-1,4-diazepinium perchlorate (G). Solutions of 0.39 g (0.001 mol) of 1,1,5,5-tetramethyl-3-(3,4,5-trimethoxyphenyl)-1,5-diazapentadienium perchlorate **E** in 15 mL of acetonitrile and 0.10 mL (0.001 mol) of *N,N′*-dimethylethane-1,2-diamine in 15 mL of acetonitrile were added simultaneously drop by drop to boiling acetonitrile (15 mL).[17] The resultant yellow solution was refluxed at 85 °C for 5 h. After cooling, the solvent was evaporated under vacuum, and the residue was kept cold overnight. The precipitate was washed with dichloromethane, recrystallized from dry ethanol, and dried in a desiccator with P_4O_{10}.

3-(3,4,5-Trimethoxyphenyl)-5a,6,7,8,9,9a-hexahydro-1H-benzo[b-1,4] diazepinium perchlorate (H). Solutions of 0.39 g (0.001 mol) of 1,1,5,5-tetramethyl-3-(3,4,5-trimethoxyphenyl)-1,5-diazapentadienium perchlorate **E** in 15 mL of acetonitrile and 0.12 mL (0.001 mol) of cyclohexane-1,2-diamine in 15 mL of acetonitrile were added simultaneously drop by drop to boiling acetonitrile (15 mL).[17] The resultant yellow solution was refluxed at 83 °C for 8 h. After cooling to room temperaure, the solvent was evaporated under vacuum, and the resultant oily residue was kept cold overnight. Then 2 mL of dichloromethane was added, and the yellow precipitate was collected by filtration, washed with dichloromethane and *n*-hexane, respectively, and dried in a desiccator with P_4O_{10}.

3-(4-Phenylphenyl)-5a,6,7,8,9,9a-hexahydro-1H-benzo[b-1,4]diazepinium perchlorate (I). Solutions of 0.38 g (0.001 mol) of 1,1,5,5-tetramethyl-3-(4-phenylphenyl)-1,5-diazapentadienium perchlorate[12] in 15 mL of acetonitrile and 0.12 mL (0.001 mol) of cyclohexane-1,2-diamine in 15 mL of acetonitrile were added simultaneously drop by drop to boiling acetonitrile (15 mL). The resultant yellow solution was refluxed at 85 °C for 7 h. After evaporating the solvent under vacuum, an oily residue was obtained and mixed with 2 mL of dichloromethane. The yellow precipitate was collected by filtration, washed with hot dichloromethane and *n*-hexane, respectively, and dried in a desiccator with P_4O_{10}.

3,3′-(4-Phenylphenyl)bis(1,5-diazapentadienium) bis(tetrafluoroborate) (J). Phosphorus oxitrichloride (4.10 mL, 0.045 mol) was added to 8.25 mL (0.11 mol) of DMF at 0 °C, and the mixture was stirred at room temperature for 30 min. 1,4-Phenylendiacetic acid (purchased from Merck; 1.5 g; 0.008 mol) was added to this reagent. The mixture was refluxed at 80 °C for 7 h and then set aside in a refrigerator for 12 h. The solution was then diluted with precooled and dried ethanol (100 mL).

A solution of 5% HBF_4 (6.9 mL, 0.05 mol) in ethanol (30 mL) was added to this solution, and the mixture was set aside in a refrigerator for 12 h. The yellow crystals of **J** were collected by filtration, washed with diethyl ether, recrystallized from dry ethanol, and dried in a desiccator with P_4O_{10}.

6,6′-(,4-Phenylphenyl) bis(2,3-dihydro-1,4-dimethyl-1H-1,4-diazepinium) bis(tetrafluoroborate) (K). 3,3′-(4-Phenylphenyl)bis(1,5-diazapentadienium) bis (tetrafluoroborate) **J** (0.25 g, 0.0005 mol) in 100 mL of boiling ethanol and 0.10 mL (0.001 mol) of *N,N′*-dimethylethane-1,2-diamine in 10 mL of ethanol was added simultaneously drop by drop to boiling ethanol (15 mL). The resultant yellow solution was refluxed at 85 °C for 10 h. After cooling to room temperature, the solvent was evaporated under vacuum, and the oily residue obtained was mixed with dichloromethane (2 mL). The precipitate formed was collected by filtration, washed once with diethyl ether and three times with n-hexane, and dried in a desiccator with P_4O_{10}.

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