Monatshefte für Chemie 121, 821–828 (1990)

Monatshefte für Chemie
Chemical Monthly

Synthesis of N-Monosubstituted [2,2′-Bipyridyl]-3,3′-diamines

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Summary. [2,2′-Bipyridyl]-3,3′-diamine (**1**) reacts with ethyl benzimidate hydrochloride (**2**) to form dipyrido[1,3]diazepine **3**. Alkylation of compound **3** with alkyl halides **5** in KOH/*DMSO*/*TBAB* yields the corresponding N-alkyl-N′-benzoyl-bipyridinediamines **7** which, after hydrolysis, give N-monosubstituted bipyridinediamines **9**.

Keywords. Alkylation; Bipyridinediamines; Dipyrido[1,3]diazepines.

Synthese von N-monosubstituierten [2,2′-Bipyridyl]-3,3′-diaminen

Zusammenfassung. [2,2′-Bipyridyl]-3,3′-diamin (**1**) reagiert mit Ethylbenzimidat Hydrochlorid (**2**) zu Dipyrido[1,3]diazepin **3**. Alkylierung von Verbindung **3** liefert nach Alkylierung mit Alkylhalogeniden **5** in KOH/*DMSO*/*TBAB* entsprechende N-Alkyl-N′-benzoyl-bipyridindiamine **7**. Verseifung von **7** führt zu N-monosubstituierten Bipyridindiaminen **9**.

Introduction

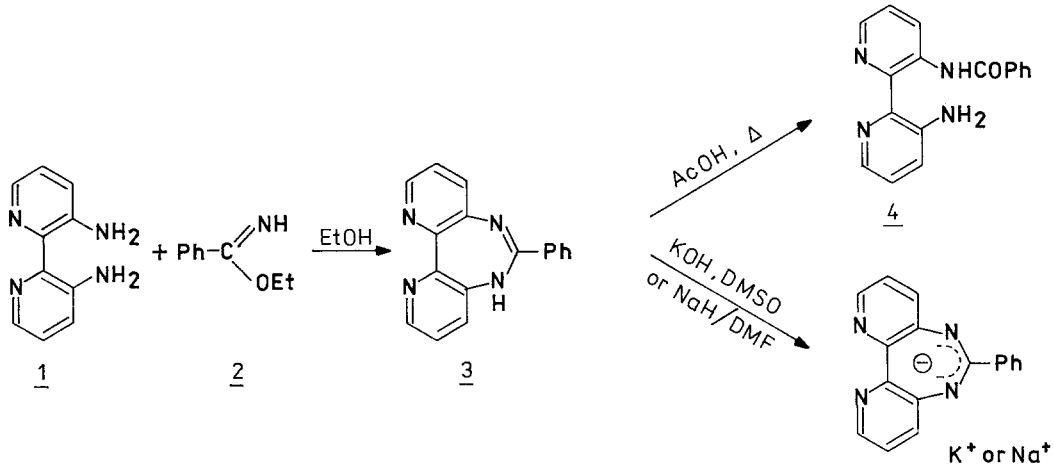
In a previous paper [1] we reported the synthesis of 6,7-dihydro-5*H*-dipyrido[3,2-d:2′,3′-f][1,3]diazepine-6-thione as a novel heterocyclic ring system. In connection with our studies on the relationship between structures and activity on the central nervous system, we required dipyrido[1,3]diazepinones substituted with one alkyl or dialkylaminoalkyl group on the nitrogen atom in the 1,3-diazepine ring. Since the direct alkylation of dipyrido[1,3]diazepinones leads to the corresponding di-substituted derivatives [2], we undertook some synthetic effort to find an efficient procedure for preparation of the desired compounds. The best results were achieved when the appropriate N-monosubstituted [2,2′-bipyridyl]-3,3′-diamines (**9**) were subjected for cyclocondensation with urea [2].

Now, we report the simple and efficient preparation of compounds **9** which are hardly available by other methods.

Results and Discussion

[2,2′-Bipyridyl]-3,3′-diamine (**1**) [1] reacts with ethyl benzimidate hydrochloride (**2**) to form 6-phenyl-5*H*-dipyrido[3,2-d:2′,3′-f][1,3]diazepine (**3**) in high yield (85%). Compound **3** undergoes easily a ring opening reaction in boiling acetic acid

to give N-benzoyl-[2,2′-bipyridyl]-3,3′-diamine (**4**). However, in alkaline media (KOH/*DMSO*) no reaction occurs and only unchanged starting material is isolated. These phenomena are evidently connected with the non-aromatic character of the 1,3-diazepine ring in compound **3** and in consequence with the high susceptibility of its C=N bond to hydrolysis. On the other hand in alkaline media compound **3** forms the fully aromatic, stable anion **3a** (deep red colour of the mixture is then observed) (s. Scheme 1).



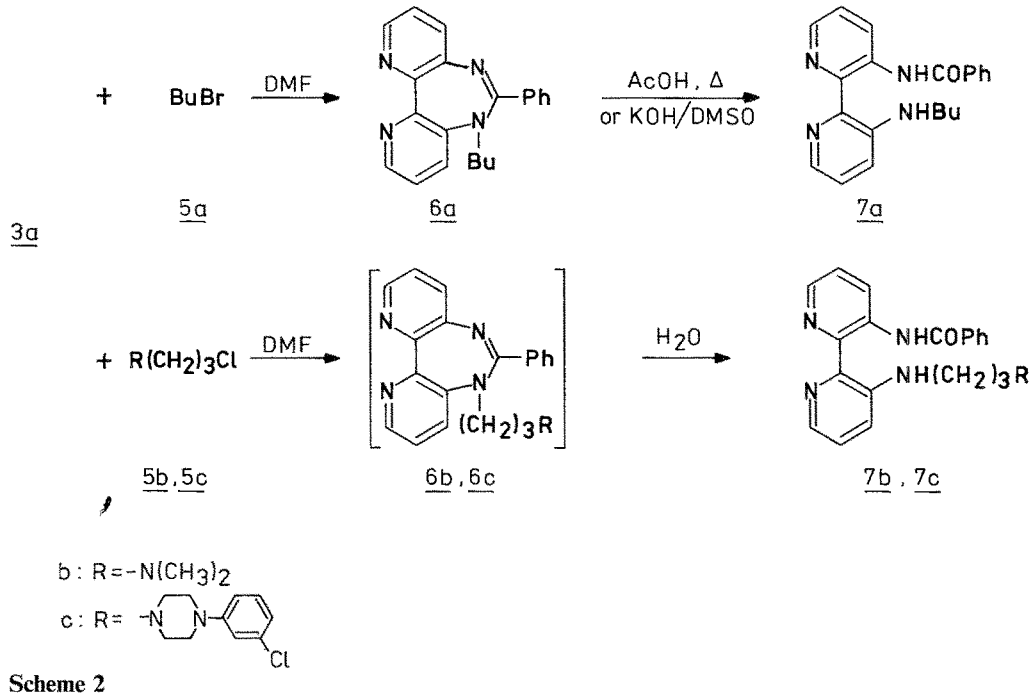
Scheme 1

On this basis we assumed, that alkylation of **3** followed by ring opening reaction and hydrolysis of the formed N-benzoyl-N′-substituted bipyridyldiamines can be used as an effective route to monoalkylated bipyridyldiamines **9**.

The alkylation was carried out by addition of alkyl halide **5** to the solution of anion **3a**, obtained earlier by the reaction of **3** with NaH in dimethylformamide (*DMF*). With butyl bromide (**5a**) as an alkylating agent, the butyl-dipyridodiazepine **6a** was obtained in good yield (76%). However, if anion **3a** was alkylated with 3-(dimethylamino)propyl chloride (**5b**) or 3-(4-*m*-chlorophenyl-1-piperazinyl)propyl chloride (**5c**) [3] the N-substituted-N′-benzoyl-bipyridinediamines **7b** and **7c** were isolated in low yields (39% and 7%, respectively), together with a considerable amount of unchanged starting material.

It seems, that the reaction of **3a** with **5b** or **5c** proceeds also with formation of substituted dipyridodiazepines **6b** or **6c**, but these compounds are less stable than butylderivative **6a** and subsequently react with water to give the corresponding compounds **7b** or **7c**. This assumption is supported by the fact that butyl-dipyridodiazepine **6a** readily transforms into the corresponding N-benzoyl-N′-butyl-bipyridyldiamine **7a** in boiling acetic acid or by heating in dimethylsulfoxide (*DMSO*) containing KOH (Scheme 2).

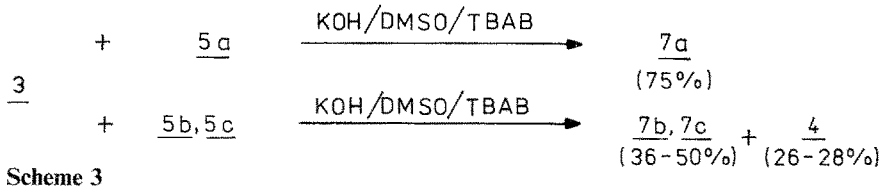
The structure of compounds **7** was assigned on the basis of ^{1}H NMR spectra. In the 60 MHz spectrum of compound **4** the signal of the proton attached to the amide nitrogen atom appears as a broad, one proton singlet at δ 15.0 ppm and both protons of the amine group show a broad, two protons singlet at 6.6 ppm. On the other hand, in the 500 MHz spectrum of **7a** the signal of the amide protons



Scheme 2

is preserved (14.94 ppm), however the signal of the amine proton appears to be a broadened, one proton triplet ($J = 4$ Hz) at 9.74 ppm. These data prove that the alkyl substituent is attached to the amine nitrogen atom.

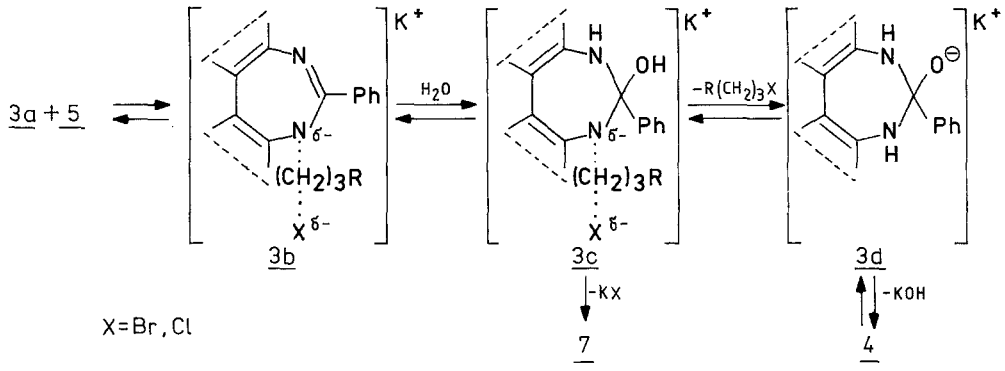
We then carried out the alkylation of dipyridodiazepine **3** with alkyl halides **5** in *DMSO* containing KOH and tetrabutylammonium bromide (*TBAB*). In the light of our previous results we anticipated that in this case the alkylation of **3** would proceed with a simultaneous ring opening to furnish the corresponding compounds **7** in a one-pot synthesis. Actually, the reaction gave N-substituted-N'-benzoyl-bipyridinediamines **7** in 35–75% yield. When the chlorides **5b** and **5c** were used as alkylating agents, besides product **7**, a considerable amount (25–30%) of un-alkylated compound **4** was also isolated (Scheme 3).



Scheme 3

To examine the possibility of dealkylation of **7b** and **7c** under the reaction conditions, we heated these compounds in *DMSO* containing KOH and *TBAB* and found that in both cases the starting material remains practically unchanged.

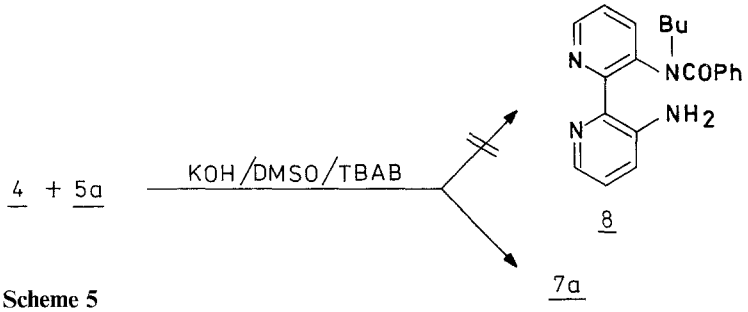
These results prompted us to rationalize the alkylation of **3** in KOH/*DMSO*/*TBAB* as shown in Scheme 4.



Scheme 4

The electrophilic attack of the alkylating agent **5** on the anion **3a** forms the intermediate **3b** containing a non-aromatic 1,3-diazepine ring, which instantly reacts with water to furnish the intermediate **3c**. This intermediate can transform into N-substituted-N′-benzoyl-bipyridinediamines **7**, or dealkylate to give **4**. The progress of the reaction depends on the nature of the leaving group *X*, e.g. if *X*=Br (an easy leaving group), **7** is practically the only product of the reaction.

The above assumption was supported by separate experiments: Compound **4** reacts with butyl bromide (**5a**) in KOH/*DMSO*/*TBAB* to give compound **7a** instead of the hypothetic isomer **8** (Scheme 5).

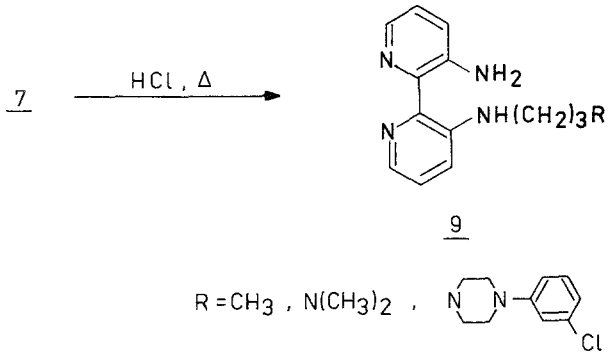


Scheme 5

4, on the other hand remains practically unchanged if KOH is replaced by triethylamine; this excludes the assumption that the amine nitrogen atom is alkylated because of its higher nucleophilic character. Rather, both experiments show that the alkylation of **4** proceeds via the intermediates **3d** and **3c** as shown on Scheme 4.

All compounds **7** were hydrolyzed in dilute HCl to give the desired N-monoalkylated bipyridinediamines **9a–c** in high yields (Scheme 6).

In conclusion it may be emphasized that cyclization of bipyridyldiamine **1** with ethyl benzimidate hydrochloride (**2**) followed by alkylation in KOH/*DMSO*/*TBAB* and hydrolysis of compounds **7** is an efficient route to N-monosubstituted bipyridyldiamines **9**, which are valuable synthons for novel compounds with potential biological activity.



Scheme 6

Experimental Part

Melting points were determined on a Kofler-type apparatus and are uncorrected. The IR spectra were recorded on a Beckman 4240 spectrophotometer (KBr, unless noted otherwise). The NMR spectra were measured on Varian EM-360 or Bruker AM-500 spectrometers and the chemical shifts are expressed in ppm (δ), with *TMS* as an internal standard. The MS spectra (− 70 eV) were recorded on LKB-9000A apparatus. Elemental microanalyses were performed by Analytical Laboratory of Institute of Organic Chemistry. Column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). The purity and identity of compounds were checked by TLC on Merck DC-Alufolien Kieselgel or Aluminiumoxyd neutral F_{254}.

DMF−dimethylformamide; *DMSO*-dimethylsulfoxide; *TBAB*−tetrabutylammonium bromide.

6-Phenyl-5H-dipyrido[3,2-d:2',3'-f][1,3]diazepine (**3**)

[2,2'-Bipyridyl]-3,3'-diamine (**1**) [1] (18.6 g, 0.1 mol) and ethyl benzimidate hydrochloride (**2**) (18.5 g, 0.1 mol) were dissolved in absolute ethanol (200 ml), then the mixture was stirred for 4 h at ambient temperature and refluxed for 1 h. After cooling the precipitate was filtered off. Yield 23.0 g (85%) from *DMF*/H_2O, m.p. above 300°C. Anal. $C_{17}H_{12}N_4$ (272.3), calcd. C 74.98, H 4.44, N 20.57%; found C 75.03, H 4.43, N 20.51%. IR: 3250–2920, 1640, 1420, 700 cm^{-1}. ^1H NMR (60 MHz, CF_3COOH): 8.7 (d, 2H, $J = 4$ Hz, H-2, H-10), 8.2–7.7 (m, 9H, H-3, H-4, H-8, H-9, phenyl). MS (*m*/e): 272 (82%), 244 (10), 169 (72), 85 (66), 83 (100).

N-Benzoyl-[2,2'-bipyridyl]-3,3'-diamine (**4**)

The mixture of dipyridodiazepine **3** (2.73 g, 0.01 mol) and acetic acid (25 ml) was refluxed for 1 h. After cooling the mixture was diluted with water (75 ml), neutralized with $NaHCO_3$ and extracted with chloroform. The extract was dried ($MgSO_4$) and evaporated to give **4**. Yield 2.18 g (75%) from benzene, m.p. 163–164°C. Anal. $C_{17}H_{14}N_4O$ (290.3), calcd. C 70.33, H 4.86, N 19.30%; found C 70.55, H 4.66, N 19.06%. IR: 3420, 3290, 2900–2700, 1655, 1575, 1530–1520, 1400, 1310, 705 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 15.0 (b.s, 1H, NHCO), 9.5 (d, 1H, $J = 8$ Hz, H-4), 8.5–8.1 (m, 4H, H-6, H-6', phenyl), 7.7–7.2 (m, 6H, H-4', H-5, H-5', phenyl), 6.65 (b.s, 2H, NH_2). MS (*m*/e): 290 (98%), 274 (6), 246 (7), 213 (100).

Alkylation of Dipyridodiazepine **3** *in* NaH/*DMF (General Procedure)*

NaH (80%, 0.45 g, 0.015 mol) was introduced to the flask under argon atmosphere, washed 3 times with hexane and diluted with dry *DMF* (25 ml). Dipyridodiazepine **3** (2.72 g, 0.01 mol) was added to the suspension and the mixture was heated at 120–130°C, until gas evolution ceased (30 min). After

cooling, the solution of corresponding alkyl halide **5** (0.015 mol) in *DMF* (5 ml) was added and the whole was heated at 100°C for 30 min. Then the solvent was evaporated in vacuo, the residue diluted with water (100 ml) and extracted with chloroform. The extract was dried, the solvent evaporated and the residue extracted again with boiling hexane to separate the product from insoluble starting material **3**. In all cases the product was purified by chromatography on a short silica gel column with chloroform.

5-Butyl-6-phenyl-5H-dipyrido[3,2-d:2',3'-f][1,3]diazepine (**6a**) (*Alkylation with Butyl Bromide* **5a**)

Yield 2.50 g (76%) from hexane, m.p. 111–112°C. Anal. $C_{21}H_{20}N_4$ (328.4), calcd. C 76.80, H 6.17, N 17.06%; found C 76.80, H 6.27, N 16.82%. IR: 2970, 1625, 1570, 1450, 1440, 1425, 780, 705 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 8.5 (m, 2H, H-2, H-10), 7.7–7.1 (m, 9H, H-3, H-4, H-8, H-9, phenyl), 3.5 (t, 2H, $J = 6$ Hz, $N-\mathbf{CH_2}-CH_2-$), 1.3 (q, 2H, $J = 6$ Hz, $N-CH_2-\mathbf{CH_2}-CH_2-$), 1.0 (m, 2H, $N-C_2H_4-\mathbf{CH_2}-CH_3$), 0.7 (t, 3H, $J = 6$ Hz, $N-C_3H_7-\mathbf{CH_3}$). MS (*m*/e): 328 (48%), 299 (22), 285 (35), 57 (100).

N-Benzoyl-N'-(3-dimethylaminopropyl)-[2,2'-bipyridyl]-3,3'-diamine (**7b**)
(*Alkylation with 3-Chloro-N,N-dimethyl-propylamine* **5b**)

Yield 1.45 g (39%), solidified oil, m.p. 72–74°C. Anal. $C_{22}H_{25}N_5O$ (375.5), calcd. C 70.37, H 6.71, N 18.65%; found C 70.38, H 6.66, N 18.58%. IR (film): 2950, 1675, 1575, 1530–1520, 1485, 1445, 1310, 705 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 14.9 (b.s, 1H, NHCO), 10.0 (b.s, 1H, NH-alkyl), 9.5 (d, 1H, $J = 8$ Hz, H-4), 8.4–8.0 (m, 4H, H-6, H-6', phenyl), 7.7–7.2 (m, 6H, H-4', H-5, H-5', phenyl), 3.3 (q. 2H, $J = 6$ Hz, $N-CH_2-\mathbf{CH_2}-CH_2-$), 2.5 (t, 2H, $J = 6$ Hz, $N-\mathbf{CH_2}-CH_2-$), 2.3 [s, 6H, $N(CH_3)_2$], 1.9 [t, 2H, $J = 6$ Hz, $-CH_2-\mathbf{CH_2}-N(CH_3)_2$]. MS (*m*/e): 375 (62%), 356 (26), 317 (100).

N-Benzoyl-N'-[3-(4-m-chlorophenyl-1-piperazinyl)propyl]-[2,2'-bipyridyl]-3,3'-diamine (**7c**)
(*Alkylation with 4-m-Chlorophenyl-1-(3-chloropropyl)piperazine* (**5c**) [3]

Yield 0.35 g (7%) from hexane, m.p. 112–113°C. Anal. $C_{30}H_{31}N_6ClO$ (527.1), calcd. C 68.36, H 5.93, N 15.94%; found C 68.16, H 5.80, N 15.63%. IR: 1670, 1570, 1525, 1240 cm^{-1}. ^1H NMR (60 MHz, *DMSO-d*$_6$): 14.8 (b.s, 1H, NHCO), 9.9 (b.s, 1H, NH-alkyl), 9.2 (d, 1H, $J = 8$ Hz, H-4), 8.4 (d, 1H, $J = 4$ Hz, H-6), 8.1–7.0 (m, 13H, H-5, H-4', H-5', H-6', phenyl, chlorophenyl), 3.6 (m, 2H, $CH_2-\mathbf{CH_2}-CH_2$), 3.2 (m, 4H, piperazine), 2.6 (m, 6H, $N-\mathbf{CH_2}-CH_2-$, piperazine), 1.9 (m, 2H, $\mathbf{CH_2}$-piperazine). MS (*m*/e): 526 (20%), 386 (31), 360 (84), 105 (100).

Ring Opening of Dipyridodiazepine **6a**

(A) In acetic acid: Compound **6a** (0.82 g, 0.0025 mol) was refluxed in acetic acid (10 ml) for 5 h. After cooling the mixture was diluted with water (50 ml), neutralized with $NaHCO_3$ and extracted with chloroform. The extract was dried, the solvent evaporated and the residue extracted with boiling hexane. After evaporation of the solvent the residue was chromatographed with chloroform on the silica gel column to give compound **7a**. Yield 0.33 g (38%).

(B) In KOH/*DMSO*/*TBAB*: Compound **6a** (0.82 g, 0.0025 mol) was added to *DMSO* (10 ml) containing powdered KOH (1 g) and *TBAB* (0.1 g). The mixture was vigorously stirred at 100°C for 3 h, then cooled, evaporated in vacuo, extracted with chloroform and worked out as above to yield 0.86 g (99%) of compound **7a**.

N-Benzoyl-N'-butyl-[2,2'-bipyridyl]-3,3'-diamine (**7a**)

M.p. 120–122°C, from hexane. Anal. $C_{21}H_{22}N_4O$ (346.7), calcd. C 72.76, H 6.40, N 16.23%; found C 72.50, H 6.25, N 16.45%. IR: 3160, 3070, 1670, 1575, 1525, 1505, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): 14.940 (b.s, 1H, NHCO), 9.735 (b.t, 1H, $J = 4.3$ Hz, NH-alkyl), 9.302 (d-d, 1H, $J = 8.4$ Hz,

1.6 Hz, H-4), 8.302 (d-d, 1 H, $J = 4.6$ Hz, 1.7 Hz, H-6), 8.100–8.077 (m, 2 H, phenyl), 7.926 (d-d, 1 H, $J = 4.4$ Hz, 1.5 Hz, H-6′), 7.555–7.505 (m, 3 H, phenyl), 7.309 (d-d, 1 H, $J = 8.4$ Hz, 4.6 Hz, H-5), 7.199 (d-d, 1 H, $J = 8.5$ Hz, 4.4 Hz, H-5′), 7.104 (d-d, 1 H, $J = 8.5$ Hz, 1.5 Hz, H-4′), 3.239–3.198 (m, 2 H, $N-CH_2-CH_2-$), 1.730 (quint., 2 H, $J = 7.1$ Hz, $N-CH_2-CH_2-CH_2-$), 1.512 (sext., 2 H, $J = 7.5$ Hz, $CH_2-CH_2-CH_3$), 1.000 (t, 3 H, $J = 7.4$ Hz, CH_2-CH_3). MS (*m*/e): 346 (57%), 317 (8), 303 (68), 105 (100).

Alkylation of Dipyridodiazepine **3** *in* KOH/*DMSO*/*TBAB* (*General Procedure*)

Dipyridodiazepine **3** (2.72 g, 0.01 mol) and the corresponding alkyl halide **5** (0.01 mol) were added to *DMSO* (50 ml) containing powdered KOH (10 g) and *TBAB* (1 g). The mixture was vigorously stirred at 100–110°C for 2 h, then an additional portion of **5** (0.01 mol) was added and the whole was stirred at 100–110°C for additional 2 h (10 h for **5c**). After heating the mixture was left for 24 h at ambient temperature, the solvent was evaporated in vacuo and the residue was diluted with water (250 ml).

Alkylation with Butyl Bromide (**5a**)

The precipitate of **7a** was filtered off and recrystallized from hexane. Yield 2.61 g (75%).

Alkylation with 3-Chloro-N,N-dimethylpropylamine (**5b**)

The mixture was extracted with chloroform, the extract dried and evaporated and the residue was washed with benzene. The crystalline compound **4** was filtered off and the filtrate was chromatographed on a silica gel column with hexane-acetone 3 : 1 to yield an additional portion of **4** (collective yield 0.80 g, 28%) and alkylated compound **7b**, yield 1.35 g (36%).

Alkylation with 4-m-Chlorophenyl-1-(3-chloropropyl)piperazine (**5c**)

The mixture was extracted with chloroform and after evaporation of the solvent the residue was diluted with hexane-acetone 3 : 1. The precipitate of alkylated compound **7c** was filtered off and the filtrate chromatographed on a silica gel column with hexane-acetone 3 : 1 to give unalkylated compound **4** (0.75 g, 26%) and **7c** (collective yield 2.64 g, 50%).

Alkylation of Compound **4** in KOH/*DMSO*/*TBAB*

The reaction of **4** (1.45 g, 0.005 mol) with butyl bromide (**5a**) (0.7 g, 0.005 mol) was carried out as above. After extraction with chloroform and evaporation of the solvent, the residue was chromatographed on a silica gel column with hexane-acetone 5 : 1 to give compound **7a** (yield 0.44 g, 25%).

N-Monosubstituted Bipyridyldiamines **9** (*General Procedure*)

Compound **7** (0.01 mol) was added to 10% HCl (50 ml) and refluxed for 4 h. After cooling the solution was alkalized with 20% NaOH and extracted with ether.

N-Butyl-[2,2′-bipyridyl]-3,3′-diamine (**7a**)

Oil, yield 97%. Anal. $C_{14}H_{18}N_4$ (242.3), calcd. C 69.39, H 7.49, N 23.12%; found C 69.55, H 7.51, N 23.00%. IR (film): 2970, 2940, 1590–1570, 1520, 1510, 1500, 1475, 1460, 1440, 1265, 1215–1200, 1150, 1070, 790, 740 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 9.3 (b.s, 1 H, NH-alkyl), 7.9 (m, 2 H, H-6, H-6′), 6.9 (d-d, 4 H, $J = 8$ Hz, 2 Hz, H-4, H-4′, H-5, H-5′), 6.4 (b.s, 2 H, NH_2), 3.0 (m, 2 H,

$N-CH_2-CH_2-$), 1.5 (m, 4 H, $CH_2-CH_2-CH_2-CH_3$), 0.95 (m, 3 H, CH_2-CH_3). MS (*m*/e): 242 (43%), 226 (14), 213 (12), 199 (100).

N-(3-Dimethylaminopropyl)-[2,2′-bipyridyl]-3,3′-diamine (**7 b**)

Oil, yield 92%. Anal. $C_{15}H_{21}N_5$ (271.4), calcd. C 66.39, H 7.80, N 25.81%; found C 66.10, H 7.97, N 25.60%. IR (film): 1 590, 1 510, 1 455, 1 445, 1 270, 1 220, 800, 735 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 9.5 (b.s, 1 H, NH-alkyl), 8.0 (m, 2 H, H-6, H-6′), 7.0 (m, 4 H, H-4, H-4′, H-5, H-5′), 6.5 (b.s, 2 H, NH_2), 3.2 (q, 2 H, $J = 6$ Hz, $CH_2CH_2-CH_2-$), 2.4 (t, 2 H, $J = 6$ Hz, $N-CH_2-CH_2-$), 2.2 [s, 6 H, $N(CH_3)_2$], 1.9 [t, 2 H, $J = 6$ Hz, $-CH_2-N(CH_3)_2$]. MS (*m*/e): 271 (51%), 213 (93), 199 (39), 187 (33), 184 (57), 170 (33), 58 (100).

N-[3-(4-m-Chlorophenyl-1-piperazinyl)propyl]-[2,2′-bipyridyl]-3,3′-diamine (**7 c**)

Oil, yield 97%. Anal. $C_{23}H_{27}N_6Cl$ (423.0), calcd. C 65.31, H 6.44, N 19.87%; found C 64.99, H 6.28, N 20.25%. IR (film): 3 490, 3 280, 2 990, 2 850, 1 600, 1 585, 1 510, 1 500–1 490, 1 450, 1 145, 755 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): 9.6 (b.s, 1 H, NH-alkyl), 7.9 (m, 2 H, H-6, H-6′), 7.0–6.7 (m, 8 H, H-4, H-4′, H-5, H-5′, chlorophenyl), 6.4 (b.s, 2 H, NH_2), 3.3 (q, 2 H, $J = 8$ Hz, $CH_2-CH_2-CH_2-$), 3.0 (m, 4 H, piperazine), 2.4 (m, 6 H, $N-CH_2-CH_2-$, piperazine), 1.7 (t, 2 H, $J = 8$ Hz, CH_2-piperazine). MS (*m*/e): 422 (51%), 407 (3), 282 (30), 269 (17), 256 (99), 226 (26), 213 (100).

Acknowledgement

Financial support of CPBR-3.8.4.1 grant is gratefully acknowledged.

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Received March 16, 1990. Accepted April 18, 1990