Pergamon

Tetrahedron 55 (1999) 1057–1062

TETRAHEDRON

Unexpected Decomposition of a Monoquarternated 4,4'-Bipyridinium Dication by Disodium Dithionite Reduction in Water

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Received 5 November 1998; accepted 25 November 1998

Abstract

Instead of the expected neutral radical the reduction of a quinoxaline bridged 4,4-bipyridinium salt by disodium dithionite (DSD) in water renders 2,3-dimethylquinoxaline and 4,4'-bipyridine. In contrast, with more electron-rich arenes used as spacer groups no decomposition products were observed. The mechanism of the chemically induced decomposition and the electrochemical properties of the starting compounds are reported.

Keywords: 4,4'-Bipyridine; Cyclic Voltammetry; Disodium Dithionite

Due to free nitrogen atoms being protonated in more acidic solvents the electrochemical reduction of monoquarternated 4,4'-bipyridinium salts ("monoquats") in water was found to be very sensitive to the pH value [1,2]. For the chemical reduction of these compounds in aqueous solution only few methods are known. Only metal complexes and no free radicals were formed using zinc under sonochemical conditions [3], while disodium dithionite (DSD) has been proved to be a suitable and strong reducing agent for 4,4'-bipyridinium salts [4].

In our study we compared the reduction behaviour of monoquarternated bis(4,4'-bipyridinium) salts in water using disodium dithionite. As spacers we used either electron-rich or electron-deficient arenes. We found an unexpected decomposition of a quinoxaline bridged 4,4'-bipyridinium salt when it was reduced in water.

The *ortho*-xylene bridged dication **1** was prepared as reported in the literature [5]. Using 2,3-bis(bromomethyl)quinoxaline and 4,4'-bipyridine the new quinoxaline bridged dication **2** was synthesized in almost quantitative yield. In the same manner, the new dication **3** was prepared as an unstable yellow solid starting from 2,3-bis(bromomethyl)benzo[b]thiophene [6] and 4,4'-bipyridine. The low yield of this reaction is attributed to the instability of the bis(bromomethyl)arene under the reaction conditions.

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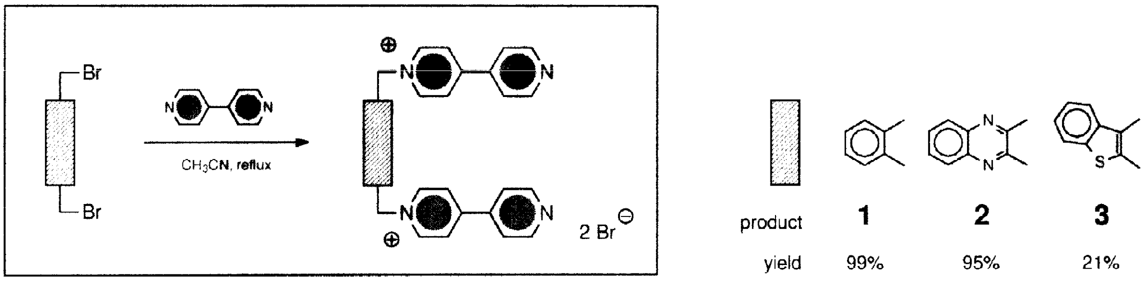
PII: S0040-4020(98)01105-3

Scheme 1



The redox potentials of compounds **1-3** were determined by cyclic and differential pulse voltammetry in DMSO and are given in Table 1. Only two redox couples were observed to form a neutral diradical and a diamagnetic dianion as illustrated for dication **3** in Figure 1. In all processes almost simultaneous transfer of two electrons is supposed. It is remarkable that the redox potentials of **2** and **3** are almost independent of the spacer, while for dication **1** more positive potentials were found. The generated dianions were unstable and decomposed to 4,4'-bipyridine and undefined spacer products [7].

Table 1. Redox potentials of monoquarternated 4,4'-bipyridinium salts[a]

Compound	$-E_1^0$	$-E_2^0$	$-E_3^0$	$-E_4^0$
1	760		823	
2	880		972	
3	881		1013	

[a] Potentials given in mV vs. Ag/AgCl (glassy carbon electrode in DMSO at 298 K).

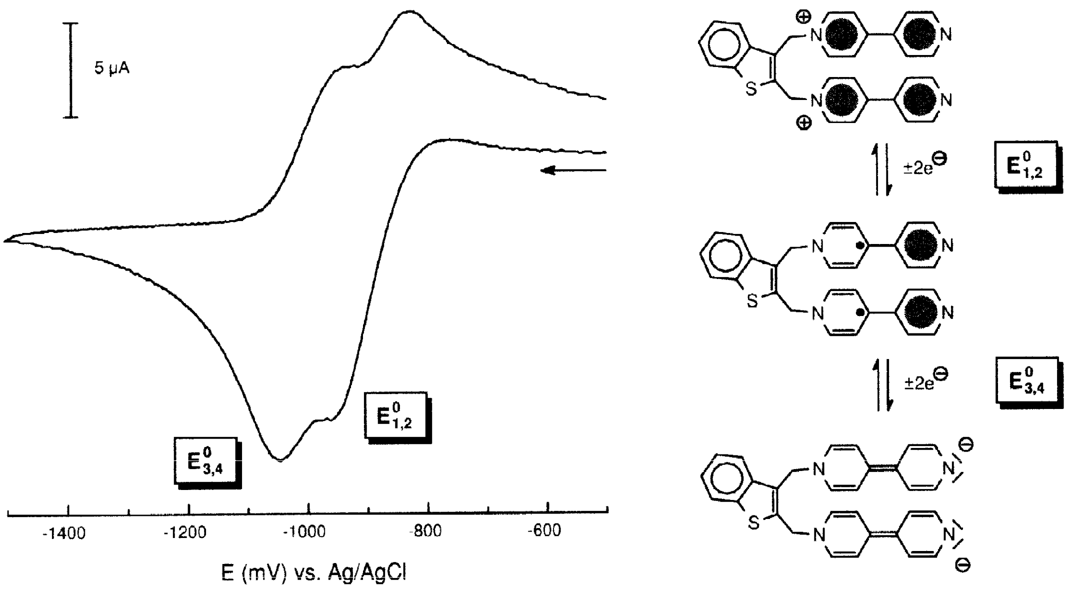
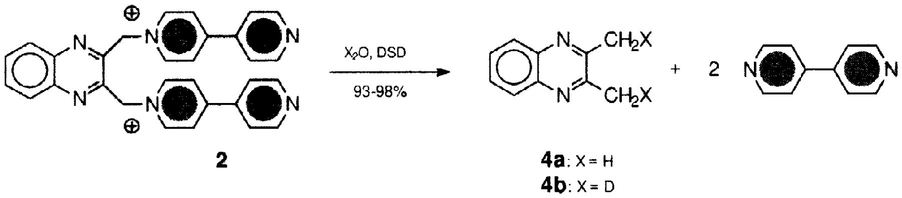


Figure 1. Cyclic voltammogram of dication **3** in DMSO (glassy carbon electrode, 1 mM, 0.05 M TBAPF$_6$, 100 mV s^{-1})

The reduction of dications **1** and **3** in water by DSD generated air-stable, deep-purple solutions with long-wave absorptions at $\lambda_{max} \approx 525$ nm. Since no signal of the corresponding radical derived from **1** was observed in the EPR spectrum, the results can be explained as reduction of the dication to the neutral diradical followed by rapid protonation and *intramolecular* π-dimerization. This is confirmed by the observation of an additional broad absorption at $\lambda_D \approx 835$ nm, which is attributed to the Davydov transition [8].

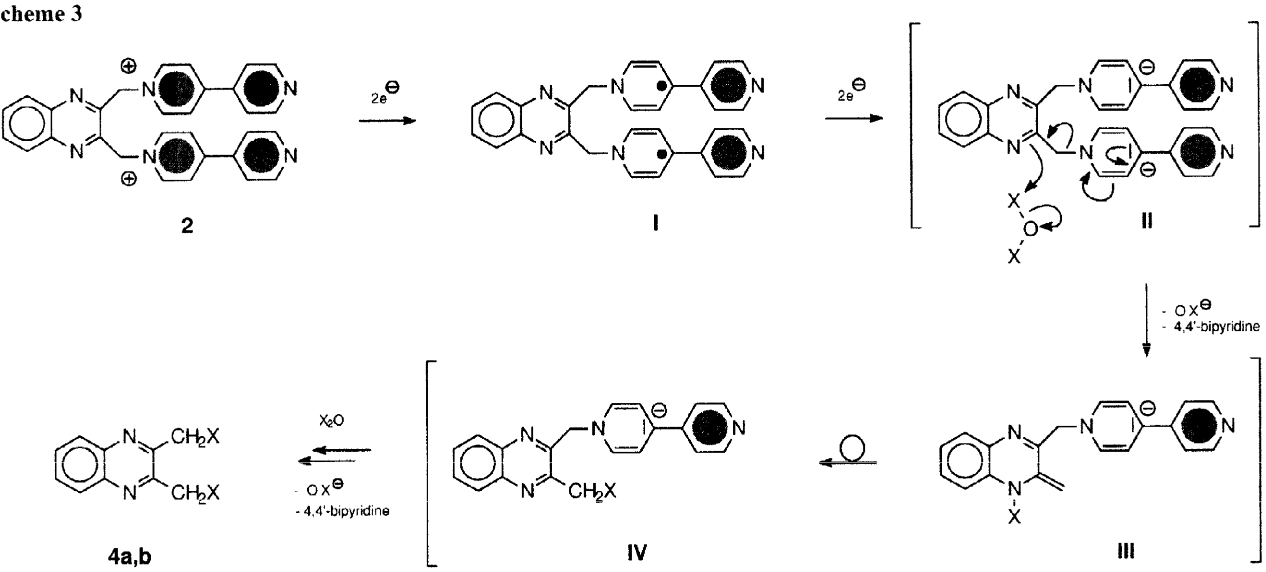
In the case of dication **2** no stable intermediates were observed. By treatment of **2**-2Br dissolved in water with DSD the colour of the solution turned to yellow, and sulfur dioxide escaped. After work-up 2,3-dimethylquinoxaline **4a** and 4,4'-bipyridine were isolated in the expected ratio of 1:2 in almost quantitative yield. A change of the proton source from water to deuterium oxide caused the formation of 2,3-dideutero-2,3-dimethylquinoxaline **4b** and 4,4'-bipyridine in 98% yield as shown in Scheme 2.

Scheme 2



For the diradicals derived from **1** and **3** no decomposition products were observed after reoxidation (O_2, 10 min; TLC, NMR). Compared with **2** the rate constants for the protonation and π-dimerization should be higher than that for the C-N-bond fragmentation. In our proposed mechanism the reduction of **2** with DSD generates the diradical **I** in the first place which will be converted into the dianion **II** (see Scheme 3). As a consecutive reaction no protonation occurs at the bipyridine moiety but the CH_2–N-bond is cleft. Probably the electron transfer and the fragmentation are simultaneous processes. The stabilized aza-allyl anion is directly protonated by the solvent (H_2O or D_2O) to enamine **III** which rearranges to **IV**. Loss of the second heterocyclic arm is leading to **4a** or **4b**.

Scheme 3



Conclusion

It could be shown that the chemical reduction of monoquarternated 4,4'-bipyridinium salts with DSD in water using electron-deficient spacers such as a quinoxaline bridge does not form stable radical species. Instead, an unexpected decomposition reaction was observed. As only reaction products 4,4'-bipyridine and 2,3-dimethylquinoxaline were isolated and characterized.

Acknowledgements. This work was supported by the Deutsche Forschungsgemeinschaft (Graduiertenkolleg "Struktur-Eigenschafts-Beziehungen bei Heterocyclen") and the Fonds der Chemischen Industrie. H. S. is grateful to the Studienstiftung des Deutschen Volkes e.V. for a fellowship.

Experimental part

General techniques: Melting points were determined on a Kofler-Boëtius apparatus and are corrected. NMR spectra were recorded on Bruker DRX-500 or AC-300P instruments with CHD_2SOCD_3 (in [D$_6$]DMSO; $\delta = 2.50$ (^{1}H), $\delta = 39.56$ (^{13}C)] and $CHCl_3$ [in $CDCl_3$; $\delta = 7.25$ (^{1}H), $\delta = 77.00$ (^{13}C)] as internal standards; signals are quoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). UV-Vis spectra were recorded on a Cary-3 double-beam spectrometer. Elemental analysis were carried out on a Carlo Erba CHN-S-Analyzer. GC-MS spectra were recorded on HP 5890 Series II with coupled IR detector HP5965B and mass sensitive detector HP5972 on a DB5MS column (J&W Scientific; 26 m × 0.32 mm, layer thickness 0.25 mm).

All reactions were monitored by thin-layer chromatography (TLC) carried out on Macherey-Nagel silica gel precoated plates Polygram Sil G/UV$_{254}$ with UV light and iodine (iodine chamber) as developing reagent. The non-aqueous alkylation reactions were performed with exclusion of moisture. Yields refer to chromatographically homogenous materials. All reagents were obtained from Aldrich, Fluka and Acros and used as received.

Electrochemical experiments were carried out on a glassy carbon electrode (diameter 3 mm) in DMSO with 0.05 M NBu_4PF_6 as supporting electrolyte under nitrogen at 25°C. As reference electrode a DMSO-filled Ag/AgCl electrode, as counter electrode a platinum sheet was used. The cyclic voltammograms were recorded on a potentiostat model 273A (EG&G Princeton Applied Research) using the software package M 270 (version 3.0).

1,1''-[2,3-Bis(methylene)quinoxaline]bis-4,4'-bipyridinium dibromide (2): To a boiling solution of 1.87 g (12.0 mmol) of 4,4'-bipyridine in dry acetonitrile (50 mL) was slowly added a solution of 0.95 g (3.00 mmol) of 2,3-bis(bromomethyl)quinoxaline in a mixture of acetonitrile and CH_2Cl_2 (60 mL, 1:1 v/v). The reaction mixture was then refluxed for two hours and after cooling to room temperature the precipitate was collected, washed with acetonitrile and air dried affording 1.93 g (95%) of **2**-2Br as colourless powder. M.p. >235°C (decomp.); $R_f = 0.37$ (silica gel; MeOH/2M aq. NH_4Cl, 3:2 v/v); UV-Vis (H_2O): λ (ε) = 320 nm (7000), 266 (47000), 241 (43700), 216 (22400); ^{1}H NMR (300 MHz, [D$_6$]DMSO, D_2O): δ = 6.73 (s, 4 H, CH_2), 7.84 (s, 4 H, quinoxaline-H), 8.16 (d, *J* = 6.0 Hz, 4 H, pyridine-3-H), 8.84 (d, *J* = 6.7 Hz, 4 H, pyridinium-3-H), 8.94 (d, *J* = 6.0 Hz, 4 H, pyridine-2-H), 9.42 (d, *J* = 6.7 Hz, 4H, pyridinium-2-H); ^{13}C NMR (75.5 MHz, [D$_6$]DMSO, D_2O): δ = 61.06 (t), 122.40 (d), 125.62 (d), 128.82 (d), 131.59 (d), 140.15 (s), 141.18 (s), 147.36 (d), 147.63 (s), 151.38 (d), 153.71 (s); $C_{30}H_{24}Br_2N_6 \cdot 2.5H_2O$ (673.4): calcd C 53.51, H 4.34, N 12.48; found C 53.44, H 4.23, N 12.52.

1,1''-[2,3-Bis(methylene)benzo[b]thiophene]bis-4,4'-bipyridinium dibromide (3): 0.48 g (1.50 mmol) of 2,3-bis(bromomethyl)benzo[b]thiophene dissolved in dry acetonitrile (20 mL) was added slowly to a boiling solution of 0.94 g (6.00 mmol) of 4,4'-bipyridine in acetonitrile (15 mL). The refluxing was continued for two hours, during this time no precipitation of the product has been observed. After hot filtration, dry ether (80 mL) was added until precipitation was complete. The solid was collected, washed with acetonitrile and air dried affording 0.21 g (21%) of the dibromide as yellow solid. A pure sample for the elemental analysis was obtained by conversion of the dibromide into the bis(hexafluorophosphate). M.p. 205°C (decomp., dibromide), 148-150°C [decomp., bis(hexafluorophosphate)]; R_f = 0.37 (silica gel; MeOH/2M aq. NH_4Cl, 3:2 v/v); UV-Vis (H_2O): λ (ε) = 264 nm (55000), 215 (35500); ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.40, 6.48 (2 s, 2 H each, CH_2), 7.49, 7.53 (2 t, *J* = 7.7, 7.5 Hz, 1 H each, benzo[b]thiophene-H), 7.86, 8.16 (2 d, *J* = 7.9, 8.0 Hz, 1 H each, benzo[b]thiophene-H), 8.00, 8.02 (2 d, *J* = 6.1 Hz, 2 H each, pyridine-3-H), 8.56, 8.65 (2 d, *J* = 6.8 Hz, 2 H each, pyridinium-3-H), 8.87 (m br, 4 H, pyridine-2-H), 9.18, 9.35 (2 d, *J* = 6.8 Hz, 2 H each, pyridinium-2-H); ^{13}C NMR (125.8 MHz, [D$_6$]DMSO): δ = 54.22 (t), 56.21 (t), 122.07 (d br), 122.58 (d), 123.49 (d), 125.67 (d), 125.81 (d), 125.92 (d), 126.61 (d), 127.27 (s), 137.47 (s), 139.05 (s), 139.24 (s), 140.75 (s), 140.79 (s), 145.05 (d), 145.60 (d), 150.97 (d), 151.01 (d), 153.16 (s), 153.47 (s); $C_{30}H_{24}F_{12}N_4P_2S \cdot H_2O$ (780.4): calcd C 46.16, H 3.36, N 7.18, S 4.11; found C 46.09, H 3.29, N 6.78, S 4.08.

Chemoreductive decomposition of (2):

a) To a stirred solution of 66 mg (0.10 mmol) of **2**-2Br in water (25 mL) was added 200 mg DSD (87%, 1.00 mmol). The mixture was neutralized with potassium carbonate and extracted three times with ether (25 mL each). After removal of the solvent 44 mg (93%) of colourless crystals were obtained. **4a**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.66 (s, 6 H, CH_3), 7.58, 7.90 (2 m, 2 H each, quinoxaline-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.09 (q), 128.32 (d), 128.73 (d), 141.12 (s), 153.40 (s); 4,4'-bipyridine: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45, 8.68 (2 d, *J* = 6.1 Hz, 4 H each, pyridine-3-H, 2-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 121.33 (d), 145.50 (s), 150.67 (d); ratio **4a** : 4,4'-bipyridine = 1:2;

b) 18 mg (0.024 mmol) of **2**-2PF$_6$ dissolved in a mixture of [D$_6$]DMSO and D_2O (1.5 mL, 1:1 v/v) was treated with 50 mg (0.25 mmol) of DSD. The usual work-up as described for a) afforded 11 mg (98%) of colourless crystals. **4b**: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.66 (t, *J* = 2.2 Hz, 4 H, CH_2D), 7.64, 7.96 (2 m, 2 H each, quinoxaline-H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 22.91 (tt, *J* = 19.6, 127.4 Hz), 128.28 (d), 128.82 (d), 141.05 (s), 153.45 (s); GC-MS (*m/z*): 161 (M^++H, 10), 160 (M^+, 70), 159 (M^+-H, 10), 118 (M^+-H$_2$DC–CN, 100).

The ^{1}H and ^{13}C NMR signals for 4,4'-bipyridine were identical to those reported in a); GC-MS (*m/z*): 156 (M^+, 100); ratio **4b** : 4,4'-bipyridine = 1:2.

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