Reduction of Dipyrido Ureas *via* 6-Alkyloxydipyrido[1,2-*c*;2′,1′-*e*]imidazolium Salts

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Dipyrido uronium salts can readily be synthesized by alkylation of dipyrido ureas with Meerwein's reagent. Compared to the corresponding ureas, the uronium salts are more reactive towards basic or reducing agents like metal hydrides. Reactivity studies show that the uronium salts can react as alkylating agents towards DMSO, DBU and NaOEt along with release of the respective dipyrido ureas. In contrast, reduction of the dipyrido uronium salts with sodium borohydride or sodium trimethoxyborohydride in dry and degassed acetonitrile leads to the imidazolium salts **7a** and **7b** in moderate yields. Analysis of the by-products reveals an *in situ* carbene formation which can be reversed by using degassed but wet acetonitrile as solvent. The yield of **7b** was increased significantly by these means.

Key words: Urea, Imidazolinone, Uronium Salts, Imidazolium Salts, Reduction

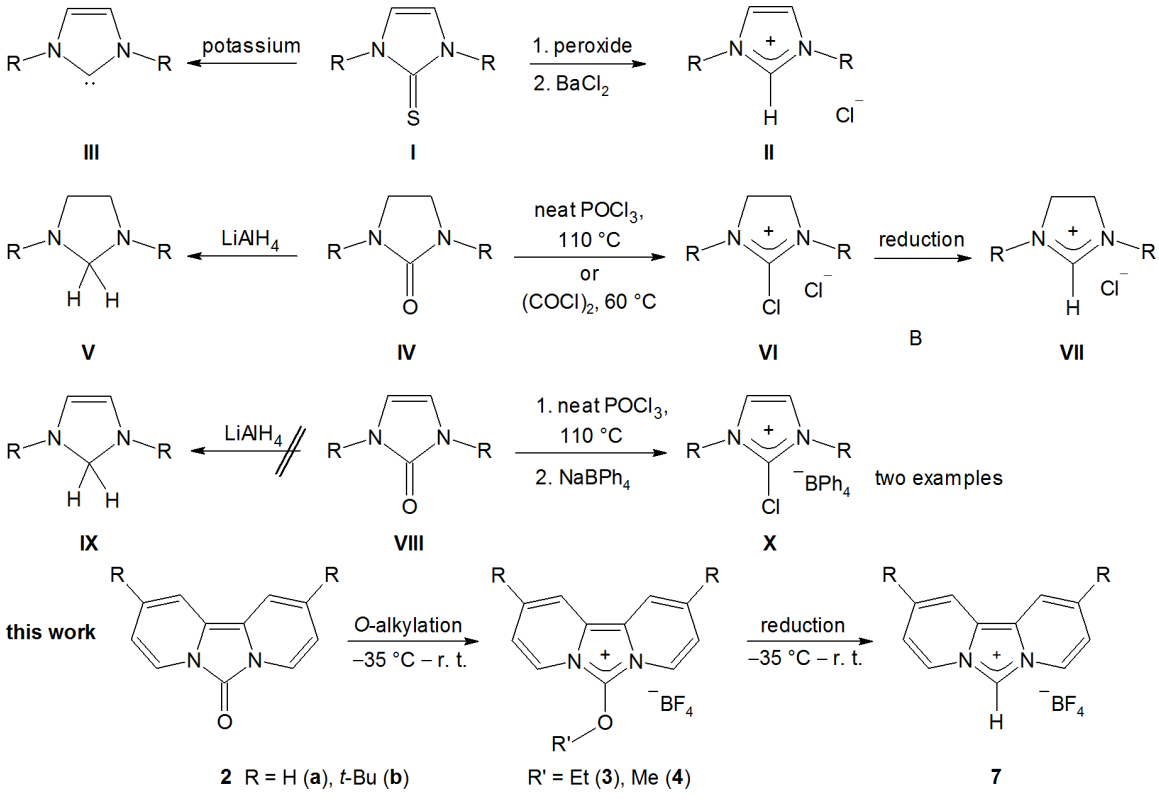
Introduction

Urea, the bisamide of carbonic acid, is one of nature's final oxidative degradation products of organisms [1]. This already demonstrates that ureas are extremely stable chemical compounds, and the reverse reaction – the reduction of ureas, is neither intended by nature nor easy to achieve in the chemist's reaction flask. A general method is not only the reduction of saturated cyclic and acyclic ureas with lithium aluminum hydride to the respective diaminomethylenes [2], but the electrochemical reduction is also known [3]. Because of our interest in dipyrido-*N*-heterocyclic carbenes [4], our goal was the use of dipyridoimidazolin-2-ones as new substrates for the preparation of dipyrido-annelated *N*-heterocyclic carbenes. This should allow us an access to the synthesis of *ortho*-substituted species. While thioureas **I** can be oxidatively desulfurated to the respective imidazolium salts **II** and subsequently converted to *N*-heterocyclic carbenes by base, or directly reduced to the carbene **III** by potassium [5], such direct reactions are not known for the respective ureas **IV** and **VIII** (Scheme 1). Imidazolidin-2-ones **IV** are more reactive towards nucleophilic attack than imidazolin-2-ones **VIII** or dipyridoimidazolin-2-ones **2** and can be readily converted to chloroformamidinium salts by reaction with neat $POCl_3$ at 100 °C or oxalyl chloride at 60 °C [6]. However, with two exceptions under harsh conditions [7], such reactivity is not known for imidazolin-2-ones **VIII** where it leads to decomposition in case of the dipyrido-annelated analogs **2**. Therefore we decided to activate dipyridoimidazolinone by alkylation to the respective uronium salts **3** and **4**. Activation of ureas by conversion into the respective uronium salts *via* alkylation is well known in literature [8], especially the route to fulvenes is a very prominent example [9]. In the case of 2-ethoxytetramethylimidazolium tetrafluoroborate, we were recently able to synthesize strongly zwitterionic fulvenes [9b]. We also reported a new two-step process to reduce imidazolinones **VIII** as well as dipyridoimidazolinones **2** to the respective imidazolium salts **7** [10]. In this paper we now present a more detailed investigation of the reaction conditions, of the mechanistic aspects as well as the structural features of the compounds involved.

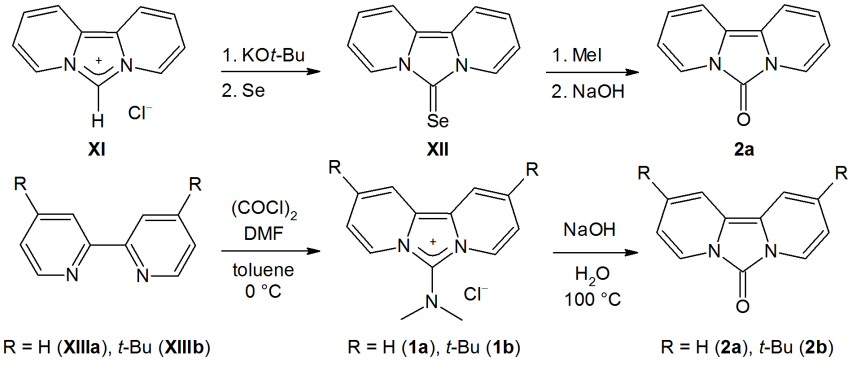
Results and Discussion

Preparation of dipyridoimidazolinones 2

Dipyridoimidazolinone **2a** was first synthesized by Weiss *et al.* by hydrolysis of an alkylselenoimid-

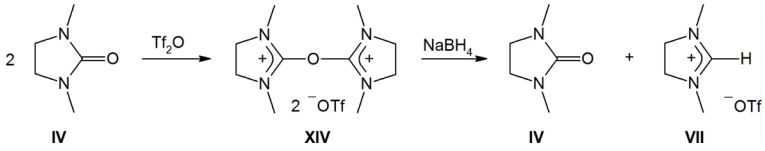


Scheme 1. Various methods for the conversion of imidazole-based ureas and thioureas to the respective imidazolium salts or carbenes.



Scheme 2. Synthesis of imidazolin-2-one **2a** according to Weiss *via* selenourea **XII**, and by hydrolysis of the guanidinium salts **1a** and **1b** which can be obtained according to Donovan and Morgan from dipyridines **XIII** [11].

azolium salt generated by alkylation and hydrolysis of the respective selenourea **XII** (Scheme 2). The selenourea was prepared by trapping the *in situ*-generated carbene (from imidazolium salt **XI**) by elemental selenium [4b]. Since we wanted to use the dipyridoimidazolinone **2** as a starting material, we needed a simple way to prepare this compound. We found that the respective guanidinium salts **1a** and **1b** can be easily prepared according to Donovan and Morgan by Vilsmeier formylation of dipyridine **XIII** [11]. We subsequently hydrolyzed **1a**, **b** under strongly basic conditions to obtain the dipyridoureas **2a** and **2b** in 74 – 79 % yield as deep-red crystalline solids after recrystallization from toluene. Alternatively, the synthesis can be run as a one-pot procedure without isolation of the guanidinium salt **1b** in an overall yield of 69 % (**2b**) and reisolation of 25 % of dipyridine **XIIIb** after workup by sublimation at 100 °C.



Scheme 3. Formation and reduction of the imidazolidine-derived bisuronium salt **XIV** leads to the imidazolidinium salt **VII** and the starting material **IV**.

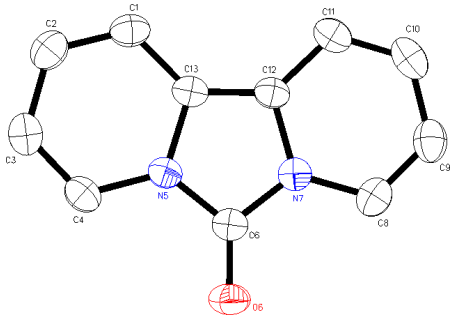


Fig. 1 (color online). Molecular structure of **2a** in the solid state as determined by X-ray structure analysis. H atoms are omitted for clarity.

The dipyrido ureas **2** are not indefinitely stable under air and should be kept under nitrogen. They are sensitive towards acid and acidic impurities, for example in dichloromethane and chloroform. As already observed for the free carbene, the *tert*-butyl substituted species **2b** is thermally more stable (T(dec.) = 199 °C) than the non-substituted dipyrido urea **2a** (T(dec.) = 125 °C) [4c]. In addition, **2b** is more stable towards air and chlorinated solvents. Although an elongation of the C=O bond could be anticipated because of a possible zwitterionic character caused by a strong stabilization of the imidazolium cation, neither the IR ν(C=O) band nor the bond lengths of the X-ray structure analyses show any unusual values. The IR band (KBr) is found at 1685 cm^{-1} (**2a**) and 1679 cm^{-1} (**2b**). This value is only slightly smaller than for *N*,*N*′-diphenylimidazolin-2-one (1690 cm^{-1}, KBr) [12] or for the saturated *N*,*N*′-diphenylimidazolidin-2-one (1690 cm^{-1}, KBr) [13].

In the solid state the C=O bond lengths have values of 1.235(2) Å (**2a**) and 1.251(2) Å (**2b**), which clearly corresponds to an albeit slightly elongated C=O double bond. Fig. 1 shows the molecular structure of **2a** while Fig. 2 shows the packing motif of **2b** in the crystal.

Attempts to reduce the dipyrido urea **2** with sodium borohydride or lithium aluminum hydride failed. The reaction with $POCl_3$ to form the 6-chlorodipyridoimidazolium salt also failed due to decomposition, as well as the reaction with Lawesson's reagent to obtain the respective thiourea.

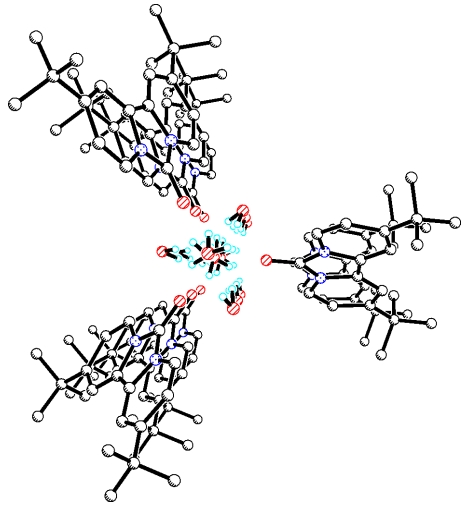
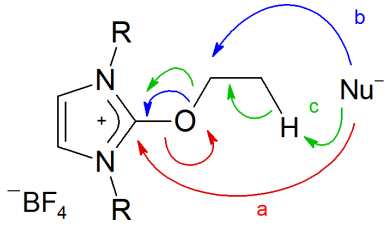


Fig. 2 (color online). Arrangement of the molecules of **2b** in the crystal as determined by X-ray structure analysis. H atoms (except in H_2O) are omitted for clarity.

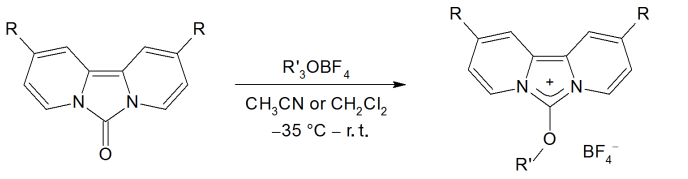
Synthesis of 6-alkoxy-dipyrido[1,2-c;2′,1′-e]imidazolium salts ***3***

Stang *et al*. reported that imidazolidinone **IV** can be activated by trifluoromethanesulfonic anhydride to obtain the bisuronium salt **XIV** (Scheme 3) [14]. This compound can be reduced with $NaBH_4$ to obtain the respective urea **IV** and the imidazolium salt **VII**. To avoid loss of half of an equivalent of the imidazolinone (although it could be recovered), we propose that *O*-alkylation of the respective urea and subsequent reduc-

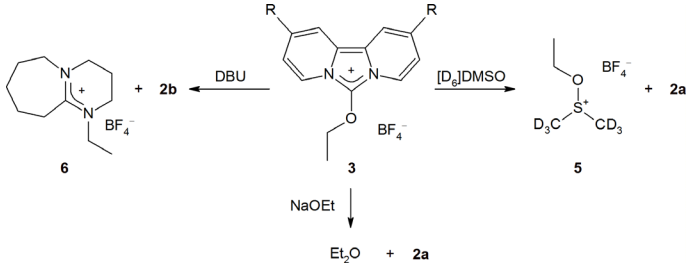


a: substitution at C-2, release of ethoxide, *e. g.* Cp-Li [9b]
b: attack at ethyl C-1, release of urea
c: deprotonation at ethyl C-2, elimination of urea and ethylene (not observed so far)

Fig. 3 (color online). Possible reaction sites for (basic) nucleophiles at 2-ethoxyimidazolium salts.



Scheme 4. Activation of dipyrido ureas **2a** and **2b** with Meerwein's reagent leads to the uronium salts **3a**, **b** and **4a**, **b**.



Scheme 5. Reactivity of the 6-ethoxy-dipyridoimidazolium salts **3** (R = H, *t*-Bu) as ethyl cation transfer agents.

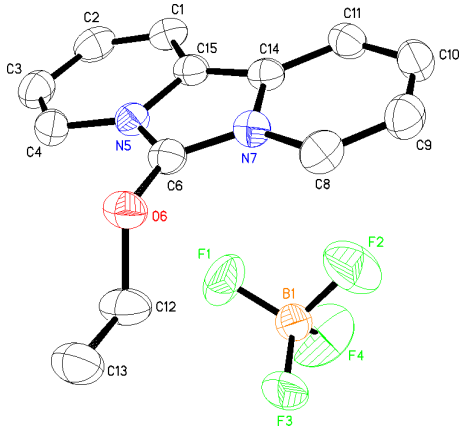


Fig. 4 (color online). Molecular structure of the dipyrido uronium salt **3a** in the solid state as determined by X-ray structure analysis. H atoms are omitted for clarity.

tion (Fig. 3, Nu^- = "H^-") could lead to the desired imidazolium salt if the hydride attack would occur at the uronium atom C-2 (pathway a) while nucleophilic substitution at the alkyl-C-atom would lead to the undesired alkane (pathway b) (or alkene, if deprotonation would occur, pathway c) along with one equivalent of imidazolin-2-one.

Preparation of the uronium salts with Meerwein's reagent trialkyloxonium tetrafluoroborate (R_3OBF_4) turned out to proceed in a straightforward way [8] (Scheme 4). The starting materials were combined at −35 °C in acetonitrile (R = Et) or dichloromethane (R = Me) and allowed to warm up to r. t. with stirring overnight. After removal of the solvents *in vacuo*, the uronium salts remained as green (**3a**, **4a**), dark-green (**3b**) or orange (**4b**) crystalline solids that need to be stored and handled under argon. While the *tert*-butyl-substituted dipyridoimidazolinone **2b** is thermally more stable than compound **2a**, the stability is inverted in case of the uronium salts. The H-substituted dipyridouronium salts decompose only above 144 °C (**3a**) and 136 °C (**4a**), while the *tert*-butyl-substituted uronium salt already decomposes at 75 °C (**3b**). Uronium salt **4b** has a melting point of 83 °C.

Structurally the uronium salts **3a**, **3b** and **4a** show similar bond angles and bond lengths. Fig. 4 shows the molecular structure of the dipyrido uronium salt **3a** in the solid state. The C–O bonds of the uronium units measure between 1.3194(2) (**3b**) and 1.326(3) Å (**4a**), clearly indicating a single bond character. The N–C–N angles of 107.5(4)° (**4a**) and 107.8(2)° (**3a**) are significantly increased compared to the respective urea (103.85(12)°, **2a**) and resemble those of the imidazolium salts **7** (*vide infra*). The alkoxy groups are oriented perpendicular to the dipyridoimidazolium plane with a C–O–C angle of 115 – 116°.

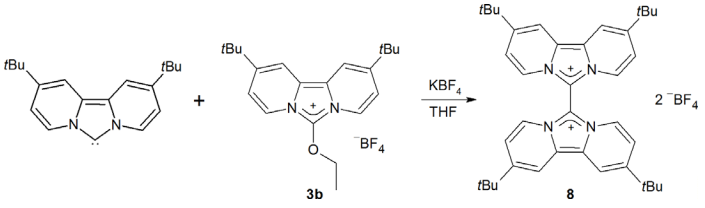
Reactivity of 6-alkoxy-dipyrido[1,2-c;2′,1′-e]imidazolium salts

Due to the high stability of the urea moiety, the uronium salts turned out to act as weak alkylating agents. In [D_6]dimethylsulfoxide, an ethyl cation transfer from the uronium salt **3a** to [D_6]DMSO with formation of the dimethylsulfoxonium salt **5** can be observed (Scheme 5). A color change from green to reddish

Table 1. Conditions applied for the reduction of **3b**.

Entry	Reducing agent	Molar equivalents	Solvent	Yield of **7b**[a] (%)	Side products[b]
1	$NaBH_4$	0.25	CH_3CN abs.	20[c]	*t*-Bu-bipy
2	$NaBH_4$	0.25 + 0.25	CH_3CN abs.	37	**8**, *t*-Bu-bipy, **2b**
3	$NaBH_4$	4 × 0.06 + 0.25	CH_3CN abs.	46	**8**, *t*-Bu-bipy, **2b**
4	$NaBH_4$	0.5	CH_3CN abs.	43	**8**, *t*-Bu-bipy, **2b**
5	$NaBH_4$	10	CH_3CN abs.	33	*t*-Bu-bipy, **8**
6	$NaBH_4$	0.25 + 0.25	CH_3CN + 1 eq. H_2O	32	*t*-Bu-bipy, **8**, **2b**
7	$NaBH_4$	0.25 + 0.25	CH_3CN (non-dried)	65(49)[d]	*t*-Bu-bipy (38 %)[d], **2b**
8	$NaBH_4$	0.25 + 0.25	CH_3CN (degassed) + 1 % H_2O (degassed)	89(77)[d]	**2b** (9 %), traces of **8**, *t*-Bu-bipy,
9	$NaB(OMe)_3H$	1	CH_3CN abs.	46[c]	*t*-Bu-bipy, **8**
10	$NaB(OMe)_3H$	10	CH_3CN abs.	0	*t*-Bu-bipy
11	KH	1	CH_3CN abs.	0	**2b**, *t*-Bu-bipy
12	DIBAL-H	1	CH_3CN abs.	0	*t*-Bu-bipy

[a] Yields were determined by ^1H NMR spectroscopy and refer to the total amount of all products observed in the NMR spectra; [b] amount of side products in decreasing order; [c] incomplete conversion of the starting material **3b**; [d] isolated yields. *t*-Bu-bipy: 4,4′-di-*tert*-butyl-2,2′-bipyridine.



Scheme 6. Reaction of *in situ*-generated carbene with the uronium salt **3b** leads to the formation of bisimidazolium salt **8**.

brown indicates the presence of the dipyrido urea **2a**. The *O*-methyluronium salts **4** show analogous reactivity. Therefore DMSO and tetrahydrofuran (slow polymerization) have to be avoided as solvents for dipyridouronium salts; acetone or acetonitrile are the preferred solvents.

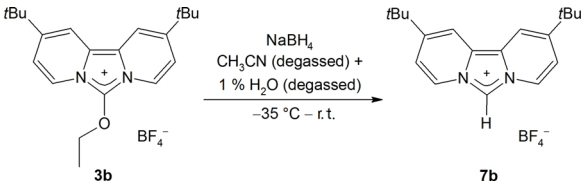
The alkylating properties are also observed when the uronium salt **3b** is reacted with the formamidine base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene). Reaction of **3b** with DBU in tetrahydrofuran does not lead to a deprotonation at the ethyl group and elimination of ethylene, but to an ethyl cation transfer to DBU. Product **6** was confirmed independently by generating **6** from DBU with triethyloxonium tetrafluoroborate in tetrahydrofuran. Reaction of the uronium salt **3a** with the strong base NaOEt resulted also in an ethyl cation transfer with formation of diethyl ether and the imidazolone **2a**.

If less strong and more sterically demanding bases are applied, like Cp-Li, the ethoxy group serves as a leaving group, and fulvene formation is observed, as we have shown in the case of 2-ethoxytetramethylimidazolium tetrafluoroborate [9b]. Therefore it was not clear if the reduction with metal hydrides would lead to the desired imidazolium salts **7** (Fig. 3, pathway a) or to the undesired formation of ethane and the urea (pathway b).

Preparation of dipyrido[1,2-c;2′,1′-e]imidazolium salts

The reduction of the ethoxy-imidazolium salts **3** turned out to be quite sensitive towards the applied conditions. We tested various metal hydrides for the reduction of **3b** in dried and degassed acetonitrile and found that only $NaBH_4$ and $NaB(OMe)_3H$ led to the desired product **7b**, however, in not more than 46 % yield. The main side products were di-*tert*-butyldipyridine **XIIIb**, urea **2b** and a compound that turned out to be the bisimidazolium salt **8**. Bisimidazolium salts in general are known for various imidazoline and imidazolidine derivatives including a bis(dipyridoimidazolium) salt described by Jellen [15]. Other reducing agents like potassium hydride or di-*iso*-butylaluminum hydride turned out to be inferior. Table 1 gives an overview of the applied conditions. KH led to imidazolin-2-one **2b** and di-*tert*-butyldipyridine **XIIIb** (entry 11), while in case of DIBAL-H only formation of di-*tert*-butyldipyridine **XIIIb** was observed.

Formation of the bisimidazolium salt **8** could be a result of an *in situ* carbene formation by reaction of the imidazolium salt with the basic metal hydrides and a subsequent nucleophilic attack at the uronium salt (Scheme 6). A similar reaction leading to bisimidazolium salts was reported by Kuhn *et al.* for the



Scheme 7. Optimized conditions for the reduction of the ethoxyimidazolium salt **3b**.

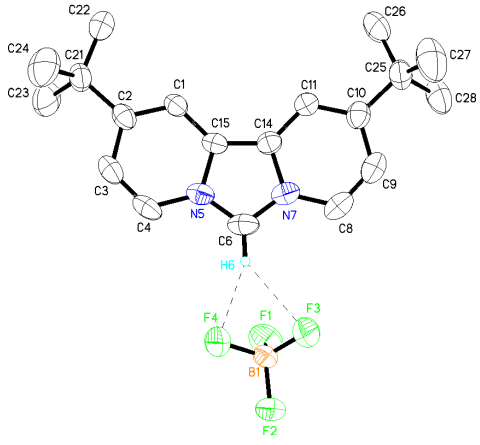


Fig. 5 (color online). Molecular structure of the dipyridoimidazolium salt **7b** in the solid state as determined by X-ray structure analysis. H atoms (except for H6) are omitted for clarity.

reaction of tetramethylimidazolin-2-ylidene with a 2-fluorotetramethylimidazolium salt [16]. Slow deprotonation of the formed imidazolium salts **7** would also explain why more (0.5 eq.) $NaBH_4$ is needed to achieve full conversion of the starting material than theoretically expected (0.25 eq.).

To avoid the formation of side products caused by an *in situ*-generated free carbene we used non-dried acetonitrile to achieve an immediate protonation of the free carbene back to the imidazolium salt **7b** by residual water. As a result, formation of the bisimidazolium salt **8** could be suppressed; however, formation of some dipyridine **XIIIb** and imidazolinone **2b** was still observed. After workup the imidazolium salts were isolated in 47 % (**7a**, cocrystallized with 0.4 eq $NaBF_4$) and 49 % (**7b**) yield. In addition, 32 % of dipyridine **XIIIa** and 38 % of di-*tert*-butyldipyridine **XIIIb** could be recovered. As oxygen is capable to react with carbenes to form ureas, we finally used degassed acetonitrile and added 1 % of deionized and degassed water. Under these optimized conditions (Scheme 7), the reaction became very clean, and the product **7b** could be isolated in 77 % yield as a yellow crystalline solid.

The molecular structure of the *tert*-butyl substituted imidazolium tetrafluoroborate **7b** in the solid state (Fig. 5) shows the BF_4^- counterion to be coordinated to the acidic imidazolium proton 6-H *via* two fluorine atoms with distances of F3···H6 = 2.403 Å and F4···H6 = 2.225 Å. The N5–C6–N7 angle measures 107.0(2)°, which is a typical value for dipyridoimidazolium salts. The other bond lengths and angles are similar to those that have been reported before [4a].

Conclusion

In conclusion we found a new and mild synthetic route to dipyridoimidazolium salts starting from dipyridoimidazolin-2-ones *via* reduction of the respective uronium salts that are readily available by alkylation of the ureas with Meerwein's reagent. The uronium salts themselves turned out to act as alkylating agents when reacted with weak bases like DMSO or DBU or strong bases like NaOEt accompanied by the formation of one equivalent of dipyrido urea. With strong metal hydrides like KH the uronium salts also react to form urea, while softer reagents like $NaBH_4$ or $NaB(OMe)_3H$ react according to a nucleophilic substitution at the uronium C-6 atom with formation of the imidazolium salts.

Experimental Section

Unless otherwise noted, all reactions were carried out under an atmosphere of dry argon using standard Schlenk techniques or were performed in a nitrogen-filled glovebox. All solvents were dried according to standard procedures and saturated with argon prior to use [17]. Chemicals used were obtained from commercial suppliers and used without further purification. ^1H and ^{13}C NMR spectra were recorded using Bruker ARX 250, DRX 300, or DRX 500 spectrometers. ^1H and ^{13}C chemical shifts are reported in ppm and calibrated to TMS on the basis of the residual proton signal of the solvent as an internal standard (^1H NMR: 2.49 ppm, [D_6]DMSO; 2.05 ppm, [D_6]acetone; 1.94 ppm, [D_3]acetonitrile; 1.73 ppm, [D_8]THF; ^{13}C NMR: 39.5 ppm, [D_6]DMSO; 29.8 ppm, [D_6]acetone; 25.5 ppm, [D_8]THF; 1.4 ppm, [D_3]acetonitrile). Assignments of ^{13}C NMR spectra were made with the aid of 2D correlation spectra. All NMR spectra were acquired at r. t. Mass spectra were recorded on a Jeol JMS-700 instrument with NBA (nitrobenzyl alcohol) as matrix or on a Bruker ApexQe Apollo II FT-ICR mass spectrometer. Infrared spectra were recorded using a Bruker Equinox 55 FT-IR spectrometer. Melting points were determined with a Büchi B 540 apparatus. Elemental analyses were performed by the Mikroanalytisches Laboratorium der Chemischen Institute der Universität Heidelberg.

*6-Dimethylaminodipyrido[1,2-c;2′,1′-e]imidazolium chloride (**1a**)*

Under argon atmosphere 500 mL of dry toluene is added to a flame-dried flask. At 0 °C 8.21 mL (7.72 g, 105 mmol) of *N*,*N*-dimethylformamide and 8.25 mL (12.2 g, 96.0 mmol) of oxalyl chloride are added. The reaction mixture is stirred at 0 °C until gas formation has ceased. Then, 15.0 g (96.0 mmol) of 2,2′-bipyridine is added, and after a short time a green solid is formed. After 30 min at 0 °C 6.7 mL (4.9 g, 48 mmol) of triethylamine is added, and after stirring for 1 h the reaction mixture is allowed to warm to r. t. The solid is filtered, washed with 500 mL of dry toluene and dried *in vacuo*. Then, the raw product is dissolved in 200 mL of water and brought to pH = 11 with conc. aqueous NaOH at 0 °C. A solid is formed, which is extracted with 3.5 L of diethyl ether. The aqueous phase is brought to pH = 5 with diluted aqueous HCl to avoid alkaline hydrolysis of the product, and the water is evaporated *in vacuo*. The residue is extracted three times with 200 mL of ethanol, and after evaporating the solvent and drying the light-green solid *in vacuo*, 15.2 g (64 %) of **1a** is obtained. From the organic phase 5.28 g (35 %) of 2,2′-bipyridine can be recovered. M. p. 171 °C (dec.). – IR (KBr): ν = 3014, 1647, 1616, 1583, 1412, 1325, 1263, 1132, 1062, 912, 750 cm^{-1}. – ^1H NMR (300.13 MHz, [D_6]DMSO): δ = 3.13 (s, 6 H, $N(CH_3)_2$), 7.44 – 7.48 (m, 2 H, 2/10-H), 7.53 – 7.58 (m, 2 H, 3/9-H), 8.71 – 8.75 (m, 4 H, 1/4/8/11-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, [D_6]DMSO): δ = 39.5 ($N(CH_3)_2$), 118.9 (C-11a/11b), 119.1 (C-1/11), 120.0 (C-3/9), 120.9 (C-4/8), 121.8 (C-2/10), 126.7 (C-6). – HRMS ((+)-ESI): m/z = 212.11818 (calcd. 212.11822 for $C_{13}H_{14}N_3$, $[M–Cl]^+$). – $C_{13}H_{14}N_3Cl \cdot 0.25\ H_2O$ (252.2): calcd. C 61.91, H 5.79, N 16.66; found C 61.94, H 5.89, N 16.88.

*6-Dimethylamino-2,10-di-tert-butyldipyrido[1,2-c;2′,1′-e]-imidazolium chloride (**1b**)*

Under argon atmosphere 100 mL of dry toluene is added to a flame-dried flask. At 0 °C 4.75 mL (4.49 g, 61.5 mmol) of *N*,*N*-dimethylformamide and 4.80 mL (7.09 g, 55.9 mmol) of oxalyl chloride are added. The reaction mixture is stirred at 0 °C until gas formation has ceased. Then, 15.0 g (55.9 mmol) of 4,4′-di-*tert*-butyl-2,2′-bipyridine is added, and after a short time a green solid is formed. After 20 min at 0 °C 3.9 mL (2.8 g, 28 mmol) of triethylamine is added, and after stirring for 1 h the reaction mixture is allowed to warm to r. t. The solid is filtered, washed with 1 L of dry toluene and dried *in vacuo*. The raw product is dissolved in 300 mL of water and brought to pH = 11 with conc. aqueous NaOH at 0 °C. A solid is formed, which is extracted three times with 750 mL of diethyl ether each. The aqueous phase is brought to pH = 5 with diluted aqueous HCl to avoid alkaline hydrolysis of the product, and the water is evaporated *in vacuo*. The residue is extracted with small amounts of acetone, filtered, and the solvent evaporated several times. After drying of the yellow solid *in vacuo*, 15.9 g (79 %) of **1b** is obtained. From the organic phase 2.84 g (15 %) of 4,4′-di-*tert*-butyl-2,2′-bipyridine can be recovered. M. p. 145 °C (dec.). – IR (KBr): ν = 3022, 2963, 2867, 1761, 1656, 1624, 1546, 1477, 1367, 1302, 1260, 1095, 1052, 804 cm^{-1}. – ^1H NMR (250.13 MHz, [D_6]DMSO): δ = 1.39 (s, 18 H, $C(CH_3)_3$), 3.11 (s, 6 H, $N(CH_3)_2$), 7.63 (br d, ^3J = 7.4 Hz, 2 H, 3/9-H), 8.50 – 8.65 (m, 4 H, 1/4/8/11-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, [D_6]DMSO): δ = 30.1 ($C(CH_3)_3$), 35.0 ($C(CH_3)_3$), 39.7 ($N(CH_3)_2$), 113.4 (C-1/11), 118.6 (C-11a/11b), 119.3 (C-3/9), 120.5 (C-4/8), 125.6 (C-6), 144.5 (C-2/10). – HRMS ((+)-ESI): m/z = 324.24346 (calcd. 324.24342 for $C_{21}H_{30}N_3$, $[M–Cl]^+$). – $C_{21}H_{30}N_3Cl \cdot H_2O$ (378.0): calcd. C 66.73, H 8.53, N 11.12; found C 66.69, H 8.50, N 10.84.

*Dipyrido[1,2-c;2′,1′-e]imidazol-6-one (**2a**)*

To a solution of 14.2 g (57.5 mmol) of 6-dimethylaminodipyrido[1,2-*c*;2′,1′-*e*]-imidazolium chloride (**1a**) in water (200 mL) 34.2 g (0.856 mmol) of NaOH is added. The reaction mixture is stirred for 1 h under reflux, and a red solid is formed. After cooling to r. t. the solid is filtered and washed with 500 mL of water and dried *in vacuo*. The solid is dissolved in toluene and dried (Na_2SO_4). After crystallization from dry toluene 8.34 g (79 %) of the air- and moisture-sensitive compound **2a** is obtained. M. p. 125 °C (dec.). – IR (KBr): ν = 3078, 3052, 1685 (C=O), 1634, 1612, 1471, 1441, 1348, 1243, 1151, 1116, 977 cm^{-1}. – ^1H NMR (500.13 MHz, [D_8]THF): δ = 6.40 – 6.48 (m, 4 H, 2/3/9/10-H), 7.46 (dt, ^3J = 7.7 Hz, $^{4,5}J$ = 1.4 Hz, 2 H, 1/11-H), 7.73 (dt, ^3J = 6.9 Hz, $^{4,5}J$ = 1.4 Hz, 2 H, 4/8-H). – $^{13}C\{^1H\}$ NMR (125.76 MHz, [D_8]THF): δ = 112.5 (C-11a/11b), 112.7 (C-2/10), 117.3 (C-3/9), 118.5 (C-1/11), 121.4 (C-4/8), 142.4 (C-6). – HRMS ((+)-EI): m/z = 184.0644 (calcd. 184.0633 for $C_{11}H_8N_2O$, $[M]^+$). – $C_{11}H_8N_2O \cdot 0.05\ H_2O$ (185.1): calcd. C 71.38, H 4.41, N 15.13; found C 71.12, H 4.34, N 15.11.

*2,10-Di-tert-butyldipyrido[1,2-c;2′,1′-e]imidazol-6-one (**2b**)*

To a solution of 10.0 g (27.8 mmol) of 6-dimethylamino-2,10-di-*tert*-butyldipyrido[1,2-*c*;2′,1′-*e*]imidazolium chloride (**1b**) in water (200 mL) 16.6 g (415 mmol) of NaOH is added. The reaction mixture is stirred for 1.5 h under reflux, and a red solid is formed. After cooling to r. t. the solid is filtered and washed with 500 mL of water and dried *in vacuo*. The solid is dissolved in toluene and dried (Na_2SO_4). After crystallization from dry toluene 6.10 g (74 %) of compound **2b** is obtained. 1.5 g (15 %) of 4,4′-di-*tert*-butyl-2,2′-dipyridine was recovered. M. p. 199 °C (dec.). – IR (KBr): ν = 3050, 2959, 2903, 2867, 1679

(C=O), 1443, 1418, 1369, 1348, 1257, 1126, 661 cm^{-1}. – ^1H NMR (300.13 MHz, [D$_8$]THF): δ = 1.28 (s, 18 H, C(CH$_3$)$_3$), 6.51 (dd, ^3J = 7.8 Hz, ^4J = 1.8 Hz, 2 H, 3/9-H), 7.31 (s br, 2 H, 1/11-H), 7.65 (dd, ^3J = 7.8 Hz, ^5J = 1.8 Hz, 2 H, 4/8-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, [D$_8$]THF): δ = 30.3 (C(*C*H$_3$)$_3$), 35.2 (*C*(CH$_3$)$_3$), 111.7 (C-1/11), 111.8 (C-11a/11b), 112.0 (C-3/9), 121.1 (C-4/8), 139.4 (C-2/10), 141.8 (C-6). – HRMS ((+)-EI): m/z (%) = 296.1888 (100) (calcd. 296.18831 for $C_{19}H_{24}N_2O$, $[M]^+$), 281.1674 (84) (calcd. 281.16449 for $C_{18}H_{21}N_2O$, $[M–CH_3]^+$). – $C_{19}H_{24}N_2O$ (296.4): calcd. C 76.99, H 8.16, N 9.45; found C 76.71, H 8.20, N 9.44.

*6-Ethoxydipyrido[1,2-c;2′,1′-e]imidazolium tetrafluoroborate (**3a**)*

To a suspension of **2a** (4.00 g, 21.7 mmol) in dry acetonitrile (200 mL) 4.13 g (21.7 mmol) triethyloxonium tetrafluoroborate is added at −35 °C under argon atmosphere. The reaction mixture is stirred overnight at r. t., and after evaporating the solvent and drying the green residue *in vacuo*, 6.24 g (97 %) of compound **3a** is obtained. The product was used without further purification. M. p. 144 °C (dec.). – IR (KBr): ν = 3121, 2990, 1688, 1657, 1562, 1435, 1323, 1263, 1238, 1081, 989, 854, 765 cm^{-1}. – ^1H NMR (300.13 MHz, CD_3CN): δ = 1.62 (t, ^3J = 7.0 Hz, 3 H, CH_3), 4.72 (q, ^3J = 7.0 Hz, 2 H, CH_2), 7.37 (ddd, ^3J = 9.2 Hz, ^3J = 7.0 Hz, ^4J = 1.0 Hz, 2 H, 2/10-H), 7.46 (dt, ^3J = 7.0 Hz, ^4J = 1.1 Hz, 2 H, 3/9-H), 8.32 (td, ^3J = 9.2 Hz, $^{4,5}J$ = 1.1 Hz, 2 H, 1/11-H), 8.40 (td, ^3J = 7.0 Hz, $^{4,5}J$ = 1.0 Hz, 2 H, 4/8-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ = 15.9 (CH_3), 76.3 (CH_2), 118.3 (C-11a/11b), 119.5 (C-1/11), 119.9 (C-4/8), 121.8 (C-3/9), 122.7 (C-2/10), 130.5 (C-6). – MS (FAB^+): m/z (%) = 513.4 (6) $[2M–BF_4]^+$, 213.2 (100) $[M–BF_4]^+$, 184.1 (65) $[M–BF_4–C_2H_5]^+$, 157.1 (18) $[M–BF_4–C_2H_5–CO]^+$. – HRMS ((+)-ESI): m/z (%) = 213.10225 (100) (calcd. 213.10224 for $C_{13}H_{13}N_2O$, $[M–BF_4]^+$), 513.20770 (9) (calcd. 513.20795 for $C_{26}H_{26}N_4O_2BF_4$, $[2M–BF_4]^+$). – $C_{13}H_{13}N_2OBF_4$ (300.1): calcd. C 52.04, H 4.37, N 9.34; found C 51.79, H 4.36, N 9.33.

*6-Ethoxy-2,10-di-tert-butyldipyrido[1,2-c;2′,1′-e]imidazolium tetrafluoroborate (**3b**)*

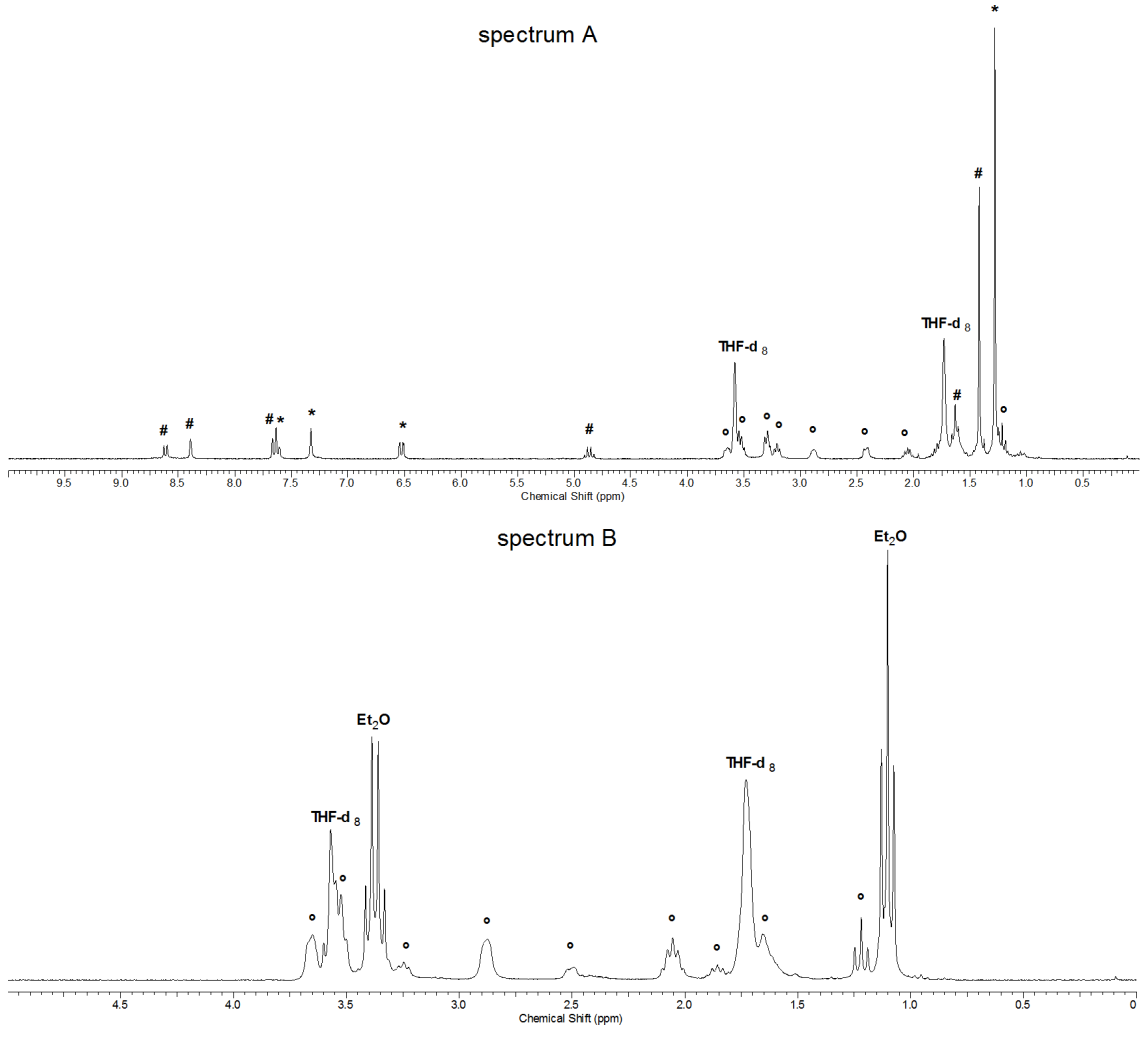
To a suspension of **2b** (500 mg, 1.69 mmol) in dry acetonitrile (20 mL) 320 mg (1.69 mmol) triethyloxonium tetrafluoroborate is added at −35 °C under argon atmosphere. The reaction mixture is stirred overnight at r. t., and after evaporating the solvent and drying the green residue *in vacuo*, 676 mg (97 %) of compound **3b** is obtained. The product was used without further purification. M. p. 75 °C (dec.). – IR (KBr): ν = 3088, 2964, 2869, 1681, 1632, 1562, 1125, 1084, 1033 cm^{-1}. – ^1H NMR (250.13 MHz, CD_3CN): δ = 1.38 (s, 18 H, C(CH$_3$)$_3$), 1.60 (t, ^3J = 7.0 Hz, 3 H, CH_3), 4.68 (q, ^3J = 7.0 Hz, 2 H, CH_2), 7.53 (dd, ^3J = 7.5 Hz, ^4J = 1.7 Hz, 2 H, 3/9-H), 8.21 (br s, 2 H, 1/11-H), 8.30 (d, ^3J = 7.5 Hz, 2 H, 4/8-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ = 16.0 (CH_3), 30.5 (C(*C*H$_3$)$_3$), 36.1 (*C*(CH$_3$)$_3$), 76.5 (CH_2), 113.7 (C-1/11), 118.1 (C-11a/b), 119.7 (C-4/8), 120.8 (C-3/9), 130.0 (C-6), 146.0 (C-2/10). – HRMS ((+)-ESI): m/z = 325.22755 (calcd. 325.22744 for $C_{21}H_{29}N_2O$, $[M–BF_4]^+$). – $C_{21}H_{29}N_2OBF_4 \cdot CH_3CN$ (453.3): calcd. C 60.94, H 7.11, N 9.27; found C 60.90, H 7.41, N 9.31.

*6-Methoxydipyrido[1,2-c;2′,1′-e]imidazolium tetrafluoroborate (**4a**)*

To a suspension of **2a** (200 mg, 1.07 mmol) in dry dichloromethane (6 mL) 161 mg (1.07 mmol) trimethyloxonium tetrafluoroborate is added at −35 °C under argon atmosphere. The reaction mixture is stirred overnight at r. t. After evaporating the solvent, extracting residual **2a** with diethyl ether, and drying of the dark-green residue *in vacuo*, 224 mg (73 %) of compound **4a** is obtained. The product was used without further purification. M. p. 136 °C (dec.). – IR (KBr): ν = 3101, 3056, 2964, 1687, 1564, 1426, 1354, 1263, 1239, 1124, 1084, 1055, 933, 745 cm^{-1}. – ^1H NMR (250.13 MHz, [D$_6$]acetone): δ = 4.67 (s, 3 H, CH_3), 7.47 (ddd, ^3J = 9.2 Hz, ^3J = 6.9 Hz, ^4J = 1.0 Hz, 2 H, 2/10-H), 7.61 (td, ^3J = 6.9 Hz, ^4J = 1.0 Hz, 2 H, 3/9-H), 8.58 (dt, ^3J = 9.2 Hz, $^{4,5}J$ = 1.0 Hz, 2 H, 1/11-H), 8.77 (dt, ^3J = 6.9 Hz, $^{4,5}J$ = 1.0 Hz, 2 H, 4/8-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, [D$_6$]acetone): δ = 65.3 (CH_3), 118.4 (C-11a/11b), 119.4 (C-1/11), 120.1 (C-4/8), 121.1 (C-3/9), 122.5 (C-2/10), 131.5 (C-6). – HRMS ((+)-ESI): m/z = 199.08662 (calcd. 199.08659 for $C_{12}H_{11}N_2O$, $[M–BF_4]^+$). – $C_{12}H_{11}N_2OBF_4 \cdot 0.04\ CH_2Cl_2$ (289.4): calcd. C 49.96, H 3.86, N 9.86; found C 49.71, H 4.03, N 9.95.

*6-Methoxy-2,10-di-tert-butyldipyrido[1,2-c;2′,1′-e]imidazolium tetrafluoroborate (**4b**)*

To a suspension of **2b** (200 mg, 0.68 mmol) in dry dichloromethane (6 mL) is added 99.8 mg (0.68 mmol) trimethyloxonium tetrafluoroborate at −35 °C under argon atmosphere. The reaction mixture is stirred overnight at r. t. After evaporating the solvent, extracting residual **2b** with diethyl ether, and concentrating the solution to dryness, the resulting residue is finely ground and dried *in vacuo*. Compound **4b** is obtained as 210 mg (75 %) of an orange solid and was used without further purification. M. p. 83 °C. – IR (KBr): ν = 3088, 2961, 2869, 1680, 1564, 1368, 1348, 1259, 1125, 1084, 1060, 1033 cm^{-1}. – ^1H NMR (300.13 MHz, [D$_6$]acetone): δ = 1.43 (s, 18 H, C(CH$_3$)$_3$), 4.65 (s, 3 H, OCH$_3$), 7.72 (dd, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 2 H, 3/9-H), 8.48 (dd, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 2 H, 1/11-H), 8.30 (d, ^3J = 7.5 Hz, ^5J = 1.0 Hz, 2 H, 4/8-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, [D$_6$]acetone):



δ = 30.4 ($C(CH_3)_3$), 35.9 ($C(CH_3)_3$), 65.3 (OCH_3), 113.5 (C-1/11), 118.1 (C-11a/11b), 119.8 (C-4/8), 120.7 (C-3/9), 130.7 (C-6), 145.8 (C-2/10). – HRMS ((+)-ESI): m/z = 311.21160 (calcd. 311.21179 for $C_{20}H_{27}N_2O$, $[M–BF_4]^+$). – $C_{20}H_{27}N_2OBF_4$ (398.2): calcd. C 60.32, H 6.83, N 7.03; found C 60.42, H 6.95, N 6.96.

*Reaction of **3b** with DBU – generation of alkylated DBU **6***

In a Young®-NMR tube 15.0 mg (0.0364 mmol) of uronium salt **3b** was reacted with 5.5 mg (0.036 mmol) of DBU in dry [D_8]THF (0.5 mL). The reaction was monitored by ^{1}H NMR spectroscopy (spectrum A). For comparison, DBU (10.0 mg, 0.0657 mmol) was reacted with Et_3OBF_4 (12.5 mg, 0.0657 mmol) in dry [D_8]THF (0.5 mL) to generate compound **6**. The reaction was monitored by ^{1}H NMR spectroscopy (spectrum B).

Besides residual starting material **3b** (#), spectrum A shows signals for imidazolone **2b** (*) and species **6** (○) which has identical peaks as species **6** (○) obtained from the second reaction (spectrum B).

*Dipyrido[1,2-c;2′,1′-e]imidazolium tetrafluoroborate (**7a**)*

6-Ethoxydipyrido[1,2-*c*;2′,1′-*e*]imidazolium tetrafluoroborate (**3a**) (2.00 g, 6.66 mmol) is dissolved in acetonitrile (80 mL) and cooled to −30 °C. Then, $NaBH_4$ (63.2 mg, 1.66 mmol) is added. The reaction mixture is kept at −30 °C for 15 h, then the same amount of $NaBH_4$ is added. The reaction is allowed to warm to r. t. After 15 h, the reaction is monitored by NMR spectroscopy. In case of an incomplete reaction, additional $NaBH_4$ (30.0 mg, 0.528 mmol) is added at −30 °C in three portions to achieve completion of the reaction. The reaction mixture is then filtered and the

Table 2. Crystal structure data for **2a**, **2b**, **3a**, **3b**, **4a**, **7a**, and **7b**.

	2a	**2b**	**3a**	**3b**	**4a**	**7a**	**7b**
Formula	$C_{11}H_8N_2O$	$C_{19}H_{28}N_2O_3$	$C_{13}H_{13}BF_4N_2O$	$C_{23}H_{32}BF_4N_3O$	$C_{11}H_{11}BF_4N_2O$	$C_{11}H_9B_{1.40}F_{5.60}N_2Na_{0.40}$	$C_{19}H_{25}BF_4N_2$
M_r	184.19	332.43	300.06	453.33	274.03	299.93	368.22
Crystal size, mm^3	$0.44 \times 0.24 \times 0.06$	$0.36 \times 0.24 \times 0.12$	$0.40 \times 0.28 \times 0.26$	$0.34 \times 0.17 \times 0.09$	$0.31 \times 0.16 \times 0.15$	$0.28 \times 0.20 \times 0.08$	$0.17 \times 0.10 \times 0.10$
Crystal system	orthorhombic	trigonal	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
Space group	*Pbca*	$P3_221$ (hexagonal setting)	*Pbca*	$P2_1/n$	*Cc*	*Cmcm*	$P2_1/c$
a, Å	14.5760(3)	11.3038(1)	10.0458(1)	9.625(5)	10.584(4)	18.681(2)	10.229(3)
b, Å	12.4720(2)	11.3038(1)	12.6761(2)	13.211(6)	9.611(4)	13.856(2)	18.553(5)
c, Å	19.2107(1)	12.5753(2)	21.2232(1)	18.490(9)	12.032(4)	24.668(3)	10.248(3)
β, deg	90	90	90	90.12(1)	90.201(7)	90	95.883(7)
V, $Å^3$	3492.35(9)	1391.55(3)	2702.60(5)	2351.1(19)	1224.0(8)	6385.2(14)	1934.6(9)
Z	16	3	8	4	4	20	4
D_{calcd}, $g\,cm^{-3}$	1.40	1.19	1.48	1.28	1.49	1.56	1.26
$\mu(MoK_\alpha)$, mm^{-1}	0.1	0.1	0.1	0.1	0.1	0.2	0.1
hkl range	$-16 \le h \le 6$ $-14 \le k \le 4$ $-22 \le l \le 2$	$-14 \le h \le 4$ $-14 \le k \le 4$ $-16 \le l \le 5$	$-12 \le h \le 2$ $-15 \le k \le 5$ $-26 \le l \le 6$	$-12 \le h \le 2$ $-17 \le k \le 7$ $-24 \le l \le 3$	$-14 \le h \le 4$ $-12 \le k \le 2$ $-16 \le l \le 5$	$-17 \le h \le 7$ $-12 \le k \le 3$ $-23 \le l \le 3$	$-11 \le h \le 1$ $-20 \le k \le 0$ $-11 \le l \le 1$
θ range data collection, deg	2.1 – 24.1	2.08 – 27.50	1.9 – 26.4	1.9 – 28.3	1.7 – 28.4	1.6 – 19.8	2.0 – 23.0
Refl. collected	26073	14358	24216	24403	6428	11228	13072
Independ. refl. / R_{int}	2788 / 0.0499	1225 / 0.0386	2760 / 0.0359	5827 / 0.0400	2986 / 0.0224	1548 / 0.0375	2699 / 0.0538
Refl. observed $[I \ge 2\sigma(I)]$	2142	1092	2128	4430	2850	1180	2082
$R1/wR2$ $[I \ge 2\sigma(I)]$	0.033 / 0.075	0.052 / 0.169	0.042 / 0.104	0.045 / 0.102	0.037 / 0.089	0.034 / 0.081	0.056 / 0.109
GoF (F^2)	1.04	1.16	1.04	1.02	1.05	1.03	1.08
$\Delta\rho_{fin}$ (max / min), $e\,Å^{-3}$	0.27 / −0.16	0.50 / −0.44	0.33 / −0.30	0.34 / −0.21	0.28 / −0.15	0.16 / −0.12	0.14 / −0.15

solvent evaporated *in vacuo*. The raw product is dissolved in small amounts of acetone, and hexane is added. The resulting solid is filtered and washed with 40 mL of diethyl ether. After recrystallization from ethanol, compound **7a** is obtained as an off-white solid (926 mg, 47 %). From the filtrate, 333 mg (32 %) of 2,2′-bipyridine can be recovered. M. p. 170 °C. – IR (KBr): ν = 3148, 3125, 3089, 3048, 3032, 1651, 1623, 1462, 1448, 1341, 1321, 1226, 1084, 750, 706 cm^{-1}. – ^1H NMR (300.13 MHz, [D$_6$]DMSO): δ = 7.53 – 7.55 (m, 2 H, 2/10-H), 7.55 – 7.60 (m, 2 H, 3/9-H), 8.65 (d, ^3J = 8.8 Hz, 2 H, 1/11-H), 8.99 (d, ^3J = 6.8 Hz, 2 H, 4/8-H), 10.24 (s, 1 H, 6-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, [D$_6$]DMSO): δ = 116.1 (C-6), 118.7 (C-4/8), 120.4 (C-2/10), 121.8 (C-11a/11b), 122.7 (C-3/9), 123.3 (C-1/11). – HRMS ((+)-ESI): m/z (%) = 169.07605 (24) (calcd. 169.07658 for $C_{11}H_9N_2BF_4$, $[M–BF_4]^+$), 425.15591 (100) (calcd. 425.15552 for $C_{22}H_{18}N_4BF_4$, $[2M–BF_4]^+$). – $C_{11}H_9N_2BF_4 \cdot$ 0.4 $NaBF_4$(299.9): calcd. C 44.05, H 3.02, N 9.34; found C 44.08, H 3.12, N 9.24.

*2,10-Di-tert-butyldipyrido[1,2-c;2′,1′-e]imidazolium tetrafluoroborate (**7b**)*

A solution of **3b** in degassed acetonitrile (100 mL) and 1 mL of degassed deionized water is cooled to −30 °C. Then, 19.4 mg (0.513 mmol) of $NaBH_4$ is added. The mixture is kept at −30 °C overnight. Then, the same amount of $NaBH_4$ is added, and the mixture is allowed to warm to r. t. After stirring for 20 h, the mixture is filtered and the solvent evaporated *in vacuo*. The raw product is dissolved in small amounts of acetone, and hexane is added. The resulting solid is filtered, and the solution is dried *in vacuo*. The residue is extracted with ethyl acetate, and the insoluble solid is added to the solid from the acetone/hexane crystallization. The solid is extracted with dichloromethane to separate the yellow product from inorganic salts. After drying *in vacuo* 580 mg (77 %) of compound **7b** is obtained. M. p. 200 °C. – IR (KBr): ν = 3138, 2961, 2869, 1663, 1487, 1369, 1261, 1124, 1084, 1053, 1012 cm^{-1}. – ^1H NMR (300.13 MHz, CD_3CN): δ = 1.41 (s, 18 H, $C(CH_3)_3$), 7.58 (dd, ^3J = 7.5 Hz, ^4J = 1.8 Hz, 2 H, 3/9-H), 8.30 (s br, 2 H, 1/11-H), 8.56 (dd, ^3J = 7.5 Hz, ^5J = 0.9 Hz, 2 H, 4/8-H), 9.54 (s, 1 H, 6-H). – $^{13}C\{^1H\}$ NMR (75.47 MHz, CD_3CN): δ = 30.4 ($C(CH_3)_3$), 36.1 ($C(CH_3)_3$), 113.9 (C-1/11), 114.5 (C-6), 121.3 (C-3/9), 123.4 (C-4/8), 147.6 (C-2/10). C-11a/b not observed. – MS ((+)-ESI): m/z (%) = 280.5 (100) $[M–BF_4]^+$, 266.5 (6) $[M–BF_4–CH_3]^+$; 251.5 (4) $[M–BF_4–2CH_3]^+$. – $C_{19}H_{25}N_2BF_4$ (368.2): calcd. C 61.98, H 6.84, N 7.61; found C 61.88, H 7.05, N 7.54.

X-Ray structure determination

X-Ray structures were obtained with a Bruker Smart diffractometer at 200 K (**2a**, **2b**, **3a**) or a Bruker APEX diffractometer at 295 K (**7a**), 200 K (**7b**), or 100 K (**3b**, **4a**), both equipped with a MoK_α radiation source (λ = 0.71073 Å) and a graphite monochromator. Intensities were corrected for Lorentz and polarization effects, and empirical absorption corrections were applied using the SADABS program [18] based on the Laue symmetry of the reciprocal space. Structure solutions and refinements were carried out with the SHELXTL program system [19] using Direct Methods for structure solution and full-matrix least-squares routines on F^2 for refinement. Crystal data and numbers pertinent to data collection and structure refinement are summarized in Table 2.

CCDC 771668 – 771674 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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