Novel Crossed Diels−Alder Reactions of 1-(2-Butadienyl)pyridinium Bromide

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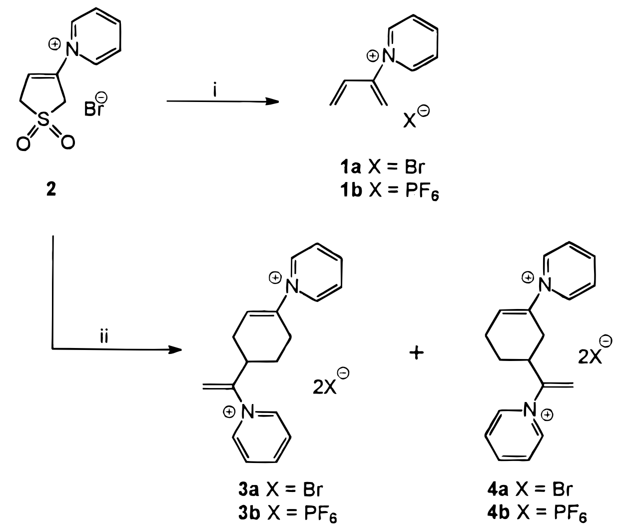
Crossed Diels−Alder cycloadditions of a positively charged diene, 1-(2-butadienyl)pyridinium bromide (**1a**), with cyclopentadiene in acetonitrile proceed stereospecifically and regioselectively. The regioselectivity of **1a** as the dienophile is especially unique.

Recently we reported the synthesis and Diels−Alder reactions of 1-(2-butadienyl)pyridinium bromide (**1a**), a diene which contains a positively charged substituent, the pyridinium group.[1] Compound **1a**, prepared in quantitative yield by thermal extrusion of SO_2 from a dilute solution of 1-(3-sulfolenyl)pyridinium bromide (**2**) in CH_3CN (0.036 M) at 140 °C for 1 h, could be converted to the corresponding PF_6 salt **1b** for ease of purification and structural identification. As we studied the thermolysis reaction of **2** more carefully, we discovered that prolonged heating of a dilute solution of **2** (0.036 M) at 140 °C for more than 16 h, or brief heating (1 h) of a more concentrated solution of **2** (0.18 M) at 140 °C, produced a trace amount of a secondary product in addition to the major product **1a**. In order to get enough sample for structural determination, we thermolyzed a concentrated solution of **1a** in CH_3CN (0.18 M) at 140 °C for 20 h. As expected, the secondary product was obtained as an oil in 95% yield, and it was determined to be a mixture of **3a** and **4a** (**3a**:**4a** = 1.7:1), the Diels−Alder dimers of **1a** (Scheme 1).

Attempts for the separation of the mixture of **3a** and **4a** totally failed due to the oily nature of these ionic compounds. This mixture was then treated with $NaPF_6$ for counterion exchange, and the resulting mixture **3b**/**4b** could be crystallized from hot water. Although a pure sample of either **3b** or **4b** could not be obtained even after several times of recrystallization, the structure of the major regioisomer was determined to be "*para*" by 2D NMR COSY experiments of the mixture. Moreover, a small piece of crystal of **3b** could be picked out from a crystalline mixture of **3b**/**4b**, and its structure was unambiguously established by X-ray crystallographic analysis.

The formation of the dimeric compounds **3a** and **4a** indicated that compound **1a** can react both as a diene and as a dienophile. Normal electron-demand Diels−Alder reactions and the dimerization of dienes bearing electron-withdrawing substituents such as an ester in **5a**,[2] a cyanide in **5b**,[3] a nitro in **5c**,[4] or a sulfonyl group in **5d**[5] at the 2-position have been reported. The dimers **6a**−**d** are results from the Diels−Alder reactions of the C_1−C_2 double bond of **5a**−**d** as the dienophile. However, the selectivity of the dimerization of **1a** is different because it is the C_3−C_4 double bond which reacts as the dienophile.

Scheme 1



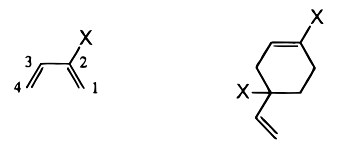
2

1a X = Br
1b X = PF_6

3a X = Br
3b X = PF_6

4a X = Br
4b X = PF_6

Conditions: (i) **2** in CH_3CN (0.036 M), sealed tube, 140 °C, 1 h
(ii) **2** in CH_3CN (0.18 M), sealed tube, 140 °C, 20 h



5 **6**

a X = CO_2Me
b X = CN
c X = NO_2
d X = SO_2Ar

Vinyl groups bearing a cationic substituent are known to react as dienophiles in Diels−Alder reactions although examples are rare.[6] For example, *N*-vinyl pyridinium tetrafluoroborate (**7**) reacts with cyclopentadiene (**8**) to give the cycloadduct **9** in good yield (eq 1).[6b]

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1996.

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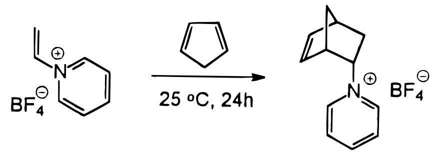
S0022-3263(96)01480-6 CCC: $12.00



(eq 1)

7 **9**

It is curious why in **1a** the C_1-C_2 double bond is less reactive than the C_3-C_4 double bond, unlike those in **5a**−**d** or 2-nitro-3-methyl-1,3-butadiene.[7] Preliminary theoretical investigation shows that the molecular orbital (MO) coefficients of HOMO and LUMO of **5b** do have larger values on the C_1-C_2 double bond. However, this is not so for compound **1a**. For **1a**, the HOMO has larger MO coefficients on the C_3-C_4 double bond than on the C_1-C_2 double bond, but the trend is reversed in LUMO+2.[8] Therefore, it is not clear whether the regioselectivity of the Diels−Alder dimerization of **1a** can be rationalized by the relative size of the MO coefficients. On the other hand, it was found that the dihedral angle of the C_1-C_2 double bond and the pyridinium plane is around 55° for cisoid **1a** and 90° for transoid conformer. The ortho hydrogens of the pyridinium ring can thus exert steric hindrance on the C_1-C_2 double bond against the approach of a diene during the Diels−Alder reaction. Hence, the unique behavior of **1a** seems to originate from steric reasons.

The fact that compound **3a** was the major Diels−Alder dimer from **1a** indicates that the pyridinium substituent is an effective "para"-directing group.[9] Similar para-directing property has been observed when **1a** was allowed to react with unsymmetrically substituted dienophile.[1]

The [4 + 2] dimerization reaction of **1a** and other Diels−Alder reactions[1] demonstrate that **1a** reacts well with electron-deficient dienes and dienophiles. We then wished to examine if **1a** can react in dienophilic manner with electron-rich dienes such as cyclopentadiene (**8**). Although several [4 + 2] cycloadducts are possible for the crossed Diels−Alder reaction[10] of **1a** and **8**, heating those two compounds at 140 °C for 6 h resulted in the formation of **10a** as the only product in 90% yield (Scheme 2). Compound **10a** is the cycloadduct of the apparent cycloaddition of **1a** as the diene with **8** as the dienophile. The formation of **10a** was interesting because by kinetic considerations one should predict the electron-rich molecule **8** to react as the diene and the electron-poor molecule **1a** to react as the dienophile. In addition, the regiochemistry of **10a** seemed to indicate that the pyridinium had reacted as a highly dominating "meta" director instead of a moderate "para" director as established earlier.[1] In order to examine this problem in more detail, we heated the mixture of **1a** and **8** at lower temperatures (room temp, 60 °C, or 100 °C) for different periods of time (Table 1). Under these reaction conditions, **10a** was obtained only as a minor component. The major component of these crossed Diels−Alder reactions was the bridged bicyclic compound **11**, the expected cycloadduct based on the consideration of the electronic nature of the reactants. Similar to the dimerization reaction of **1a**, it is the C_3-C_4 double bond of **1a** which reacted as the dienophile part in the crossed Diels−Alder reaction with **8**.

Scheme 2

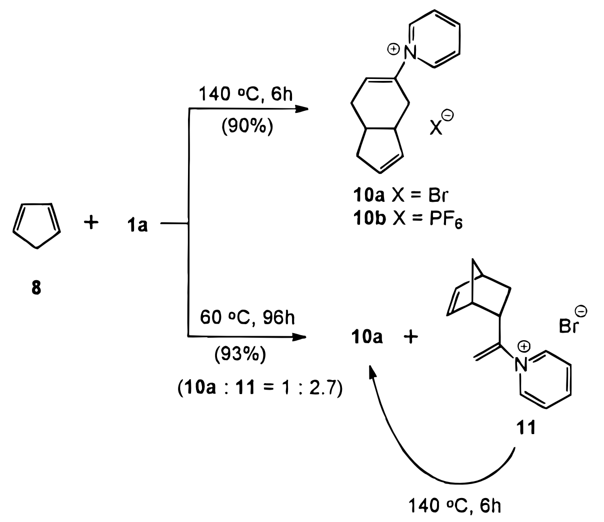


Table 1. Crossed Diels−Alder Reactions of 1a and 8 in CH_3CN under Various Conditions

entry	molar ratio (**8**/**1a**)	temp (°C)	time	products and ratio[a] **1a**	**10a**	**11**
1	10	rt	24 h	1	0.14	0.43
2	5	60	17 h	1	0.25	0.4
3	5	60	40 h	1	0.6	0.75
4	5	60	5 d	1	1.1	1.8
5	5	60	9 d	1	1.6	1.8
6	10	60	2 h	1	1.2	5
7	10	60	50 h	1	2.2	5
8	10	60	96 h	nd[b]	1	2.7
9	5	100	1 h	1	0.4	0.7
10	5	100	3 h	1	1	2
11	5	100	24 h	nd[b]	1	0.8
12	5	140	1 h	<0.05	1	0.6
13	5	140	2 h	<0.05	1	0.18
14	10	140	1 h	<0.05	1	0.5
15	10	140	6 h	nd[b]	1[c]	nd[b]

[a] The ratios of these compounds were determined by ^1H NMR spectral analyses. [b] nd: not detected. [c] Compound **10a** was the only observed product.

Compound **11** was completely converted to **10a** when it was heated at 140 °C for 6 h. One possible pathway for this conversion is the Cope-rearrangement of **11**, a process known to occur at elevated temperature in similar systems.[11,5b] The other possible pathway is the thermal equilibrium between **11** and **10a** via a Diels−Alder/retro Diels−Alder process which gave the more stable isomer **10a** as the final product. In order to differentiate the two pathways, we heated compound **11** with *N*-phenylmaleimide (5 equiv) at 140 °C for 6 h and found that the conversion to **10a** was very clean where **12** or **13** could not be detected. In another experiment, we treated a mixture of **1a**, **8**, and *N*-phenylmaleimide (1:1:3) at 140 °C for 1 h and obtained **12**[12] and **13**[13] where neither **10a** nor **11** was detected. The results of these two experiments indicate that compound **11** does not undergo retro Diels−Alder reaction under the conditions.

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(8) LUMO and LUMO+1 of compound **1a** are basically π^* orbitals of pyridinium.

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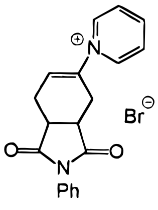
Otherwise, compounds **12** and **13** should have been formed when **11** was heated at 140 °C in the presence of excess *N*-phenylmaleimide. Therefore, the kinetic product of the cycloaddition reaction between **1a** and **8** is compound **11** which was obtained at low temperature. At higher temperatures, compound **11** undergoes a sigmatropic Cope rearrangement leading to the thermodynamically more stable isomer **10a**. Of course, the possibility that part of **10a** was produced from the direct Diels−Alder reaction of **1a** as the diene and **8** as the dienophile cannot be strictly ruled out.



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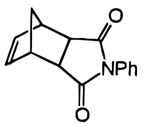
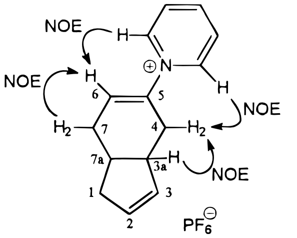
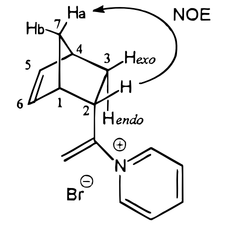


13

The structures of **10a** and **11** were assigned on the basis of chemical analyses and spectral data. Since **10a** could be obtained by the Cope rearrangement of **11**, the only possible regio- and stereochemistry assignments for these two compounds are the ones shown in Scheme 2. The NMR NOESY experiments of both **10b** and **11** are consistent with the structural assignments: (1) the C_4 methylene hydrogens of **10b** were found in close proximity to the C_{3a} allylic methine hydrogen as well as the *ortho*-hydrogens of the pyridinium; (2) the C_2 methine hydrogen of **11** was found in close proximity to one of the two C_7 bridge hydrogens, so that it should be on the exo position of the norbornene skeleton. The stereochemistry of **11** indicates a favorable secondary orbital overlap interaction of the vinylpyridinium moiety with the π-system of **8** so that endo approach took place during the cycloaddition reaction of **1a** with **8**.



NOESY correlations observed on **10b**



NOESY correlations observed on **11**

In our previous paper,[1] we described that the reaction of **2**, the precursor for **1a**, and **8** at 110 °C for 1 h produced an unidentified mixture of products. After knowing the details of the dimerization of **1a** and the crossed Diels−Alder reaction of **1a** and **8**, we reanalyzed the ^{1}H NMR spectrum of unidentified mixture of products we obtained earlier by heating **2** and **8** (20 equiv). The mixture was found to be composed of **2**, **10a**, and **11** (**2**:**10a**:**11** = 1:1.3:1.7). This observation indicates that at 110 °C, compound **2** gradually extruded SO_2 and the intermediate **1a** reacted with **8** to produce **10a** and **11**.

In summary, we have demonstrated that compound **1a** serves not only as a 2-substituted, reactive diene toward electron-deficient dienophiles in normal mode Diels−Alder reactions, but also as a monosubstituted dienophile toward cyclopentadiene in the crossed Diels−Alder reaction. The unique regioselectivity of **1a** as the dienophile is especially interesting.

Experimental Section

1-(2-Butadienyl)pyridinium Bromide (1a). A solution of 1-(3-sulfolenyl)-pyridinium bromide (**2**)[14] (414 mg, 1.5 mmol) in CH_3CN (42 mL) was heated in a sealed tube at 140 °C for 1 h. The solvent was then removed under reduced pressure to afford **1a** in nearly quantitative yield as a yellowish oil: ^{1}H NMR (D_2O, 200 MHz) δ 4.76 (d, 1H, $J = 17.3$ Hz), 5.34 (d, 1H, $J = 11.1$ Hz), 5.55 (s, 1H), 5.72 (s, 1H), 6.59 (dd, 1H, $J = 17.3$, 11.1 Hz), 8.00 (t, 2H, $J = 7.1$ Hz), 8.52 (t, 1H, $J = 7.5$ Hz), 8.71 (d, 2H, $J = 5.6$ Hz); IR (neat) 3120, 1625, 1467, 1207 cm^{-1}; FABMS (*m*/*e*) calcd for $C_9H_{10}N$ 132, found 132.

1-(2-Butadienyl)pyridinium Hexafluorophosphate (1b). A solution of **1a** (265 mg, 1.25 mmol) and $NaPF_6$ (419 mg, 2.5 mmol) in H_2O (12 mL) was stirred at room temperature for 14 h. The resulting precipitate was collected by filtration and then recrystallized from hot water to give **1b** in 83% yield. Compound **1b**: white solid, mp 144−146 °C; ^{1}H NMR (D_2O, 200 MHz) δ 4.80 (d, 1H, $J = 17.5$ Hz), 5.38 (d, 1H, $J = 11.0$ Hz), 5.58 (s, 1H), 5.76 (s, 1H), 6.63 (dd, 1H, $J = 17.5$, 11.1 Hz), 8.04 (t, 2H, $J = 7.1$ Hz), 8.56 (t, 1H, $J = 7.8$ Hz), 8.74 (d, 2H, $J = 6.5$ Hz); IR (KBr) 3135, 1631, 1601, 1476, 1387, 1270 cm^{-1}; FABMS (*m*/*e*) calcd for $C_9H_{10}N$ 132, found 132; Anal. Calcd for $C_9H_{10}F_6NP$: C, 38.98; H, 3.64; N, 5.05. Found: C, 38.54; H, 3.33; N, 4.74.

1-[4-(1-Pyridiniovinyl)cyclohex-1-en-1-yl]pyridinium Bis(hexafluorophosphate) (3b) and 1-[5-(1-Pyridiniovinyl)cyclohex-1-en-1-yl]pyridinium Bis(hexafluorophosphate) (4b). A solution of 1-(3-sulfolenyl)pyridinium bromide (**2**) (55.2 mg, 0.2 mmol) in CH_3CN (1.1 mL) was heated in a sealed tube at 140 °C for 20 h. The solvent was then removed under reduced pressure to afford the mixture of **3a**/**4a** (40.2 mg, **3a**:**4a** = 1.7:1) in 94.8% yield as a yellowish oil. A mixture of the resulting **3a**/**4a** and $NaPF_6$ (66 mg, 0.39 mmol) in H_2O (6 mL) was stirred at room temperature for 14 h and then extracted with CH_2Cl_2. After removal of the solvent under reduced pressure, the residue was recrystallized from hot water to give 39.2 mg of **3b**/**4b** (**3b**:**4b** = 3.4 :1) (70.8% yield from **2**) as white solid, mp 204−207 °C. There are essentially no overlappings of the ^{1}H NMR or ^{13}C NMR signals of the two isomers except at the pyridinium region. Therefore, the peaks of **3b** and **4b** can be assigned as follows based on the analysis of ^{1}H−^{1}H COSY and ^{1}H−^{13}C HMQC spectra as well as the relative size of the peaks of the ^{1}H NMR spectrum. ^{1}H NMR of **3b** (acetone-d_6, 500 MHz) δ 2.01−2.10 (m, 1H), 2.35−2.41 (m, 1H), 2.58−2.66 (m, 1H), 2.78−2.84 (m, 1H), 2.92−3.06 (m, 2H), 3.37−3.44 (m, 1H), 5.96 (br s, 1H), 6.00 (br s, 1H), 6.59 (t, 1H, $J = 2.1$ Hz), 8.30 (t, 2H, $J = 6.9$ Hz), 8.38 (t, 2H, $J = 6.8$ Hz), 8.79 (t, 1H, $J = 7.9$ Hz), 8.88 (t, 1H, $J = 7.9$ Hz), 9.12 (d, 2H, $J = 6.8$ Hz), 9.23 (d, 2H, $J = 6.8$ Hz); ^{1}H NMR of **4b** (acetone-d_6, 500 MHz) δ 1.84−1.93 (m, 1H), 2.22−2.29 (m, 1H), 2.50−2.60 (m, 1H), 2.75−2.80 (m, 1H), 3.05−3.15 (m, 2H), 3.48−3.55 (m, 1H), 5.96 (br s, 1H), 6.00 (br s, 1H), 6.63 (t, 1H, $J = 2.4$ Hz), 8.29 (t, 2H, $J = 6.8$ Hz), 8.35 (t, 2H, $J = 6.8$ Hz), 8.76 (t, 1H, $J = 7.9$ Hz), 8.86 (t, 1H, $J = 7.9$ Hz), 9.09 (d, 2H, $J = 6.8$ Hz), 9.18 (d, 2H, $J = 6.8$ Hz); ^{13}C NMR of **3b** (acetone-d_6, 125.7 MHz) δ 26.3, 27.9, 28.3, 37.7, 117.1, 128.1, 129.1, 129.4, 142.5, 144.2, 144.9, 147.4, 148.0, 154.0; ^{13}C NMR of **4b** (acetone-d_6, 125.7 MHz) δ 24.7, 25.5, 32.7, 39.3, 117.3, 128.2, 129.1, 129.4, 142.5, 144.2, 144.9, 147.4, 148.0, 154.0; IR (KBr) of **3b**/**4b** 3143, 3088, 1664, 1632, 1480, 1217 cm^{-1}; FABMS (*m*/*e*) calcd for $C_{18}H_{20}N_2$ 264, found 264; calcd for $C_{18}H_{20}F_6N_2P$

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(12) Compound **12** was obtained as the cycloadduct of **1a** and *N*-phenylmaleimide (see reference 1). ^{1}H NMR (D_2O, 300 MHz) δ 2.58−2.80 (m, 2H), 2.98 (d, 2H, $J = 5.2$ Hz), 3.41−3.50 (m, 1H), 3.60−3.70 (m, 1H), 6.44 (t, 1H, $J = 5.2$ Hz), 7.02−7.08 (m, 2H), 7.30−7.42 (m, 3H), 7.91 (t, 2H, $J = 7.0$ Hz), 8.42 (t, 1H, $J = 7.8$ Hz), 8.60 (d, 2H, $J = 6.2$ Hz).

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409, found 409. Anal. Calcd for $C_{18}H_{20}F_{12}N_2P_2$: C, 38.91; H, 3.68; N, 4.96. Found: C, 39.00; H, 3.64; N, 5.05.

X-ray Structure Analysis of Compound 3b. Crystal data: $C_{18}H_{20}F_{12}N_2P_2$, monoclinic system, space group $P2_1/n$; $a = 6.928(1)$, $b = 23.154(5)$, $c = 14.517(3)$ Å, $\beta = 101.07(3)$; $V = 2285.4(8)$ Å^3, $Z = 4$, $F(000) = 1120$, $D_{calc} = 1.611$ mg m^{-3}, $\mu = 2.97$ cm^{-1}. Of the 2937 reflections collected ($2\theta_{max} = 45°$), 1580 unique reflections were considered observed ($I > 2\sigma(I)$) after Lorentz polarization and empirical absorption corrections. The reliability factors converged to $R_1 = 0.067$.[15]

Crossed Diels−Alder Reactions of 1a with Cyclopentadiene (8). A sealed tube containing a CH_3CN (10 mL) solution of **1a** (61.4 mg, 0.29 mmol) and **8** (191.4 mg, 2.9 mmol) was heated at 60 °C for 96 h. After removal of the solvent, the residue was dissolved in water and then was washed with CH_2Cl_2 to remove the excess of cyclopentadiene. The aqueous layer was concentrated under reduced pressure to give 76.1 mg of the mixture of **10a** and **11** (**10a**:**11** = 1:2.7 by ^{1}H NMR spectral analysis). Column chromatography of the mixture on silica gel (elution with 5:1 CH_2Cl_2/MeOH) afforded **10a** and **11** in 19% and 48% yield, respectively. The reaction at 140 °C was carried out similarly by heating a mixture of **1a** and **8** for 6 h. After workup as described above, **10a** was obtained in 90% yield. By counterion exchange with $NaPF_6$ in aqueous solution, the crude hexafluorophosphate salt of **10b** was recrystallized from hot water to give the pure product **10b** as a white solid (84.5% yield from **1a**).

1-(3a,4,7,7a-Tetrahydro-1*H*-5-indenyl)pyridinium Hexafluorophosphate (10b): pale yellow solid, mp 143−145 °C; ^{1}H NMR (MeOH-d_4, 500 MHz) δ 2.17 (d, 1H, $J = 13.7$ Hz), 2.28 (d, 1H, $J = 17.2$ Hz), 2.50−2.72 (m, 4H), 2.86−2.97 (m, 1H), 3.26 (br s, 1H), 5.75 (s, 1H), 5.83 (s, 1H), 6.48 (s, 1H), 8.14 (t, 2H, $J = 6.8$ Hz), 8.64 (t, 1H, $J = 7.8$ Hz), 8.96 (d, 2H, $J = 6.0$ Hz); ^{13}C NMR (MeOH-d_4, 75.4 MHz) δ 29.7, 31.7, 35.4, 40.8, 45.0, 129.4, 130.8, 132.1, 135.7, 144.0, 144.4, 147.4; IR (KBr) 3144, 2929, 2847, 1634, 1477, 1357, 1219 cm^{-1}; FABMS (*m*/*e*) calcd for $C_{14}H_{16}N$ 198, found 198; FABHRMS calcd for $C_{14}H_{16}N$ 198.1282, found 198.1283.

***endo*-1-(1-Norborn-5-en-2-ylvinyl)pyridinium Bromide (11):** yellow oil; ^{1}H NMR (MeOH-d_4, 500 MHz) δ 1.14−1.19 (m, 1H, H-3*endo*), 1.45 (d, 1H, $J = 8.4$ Hz, H-7a), 1.54 (dd, 1H, $J = 8.4$, 2.2 Hz, H-7b), 2.12−2.20 (m, 1H, H-3*exo*), 2.84 (s, 1H, H-1), 2.98 (s, 1H, H-4), 3.44−3.48 (m, 1H, H-2), 5.48 (s, 1H), 5.57 (s, 1H), 6.00−6.05 (m, 1H, H-6), 6.35−6.40 (m, 1H, H-5), 8.21 (t, 2H, $J = 6.8$ Hz), 8.72 (t, 1H, $J = 7.9$ Hz), 9.03 (d, 2H, $J = 6.6$ Hz); ^{13}C NMR (MeOH-d_4, 75.4 MHz) δ 31.9, 44.2, 44.8, 46.5, 50.8, 116.6, 129.7, 132.3, 139.9, 145.2, 148.1, 155.4; IR (neat) 3064, 2970, 1626, 1471, 1338, 1221 cm^{-1}; FABMS (*m*/*e*) calcd for $C_{14}H_{16}N$ 198, found 198; FABHRMS calcd for $C_{14}H_{16}N$ 198.1282, found 198.1283.

Cope Rearrangement of 11 to 10a. A solution of **11** (27.8 mg, 0.1 mmol) in CH_3CN (3 mL) was heated in a sealed tube at 140 °C for 6 h. After removal of excess solvent, **10a** was obtained in nearly quantitative yield. The ^{1}H NMR spectrum indicated its purity to be greater than 95%.

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Supporting Information Available: ^{1}H NMR spectra of compounds **3a**/**4a**, **3b**/**4b**, **10b**, and **11**; ^{1}H−^{1}H COSY spectra of **3b**/**4b**, **10b** and **11**; ^{13}C NMR spectrum of **3b**/**4b**; ^{1}H−^{13}C HMQC spectra of **3b**/**4b**; NOESY spectra of **10b** and **11**; and the ORTEP drawing of **3b** (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[15] The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.