Syntheses and Properties of Dipyridylnorbornadienes

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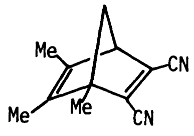
2,3-Dipyridylnorbornadienes were prepared using the Diels–Alder reaction of the HBF_4 salts of dipyridylacetylenes with cyclopentadiene. Their absorptions extend to 380 nm and are red-shifted in an acidic media. They underwent photocyclization to give quadricyclanes which reverted to norbornadienes upon heating or encountering a Co(II)–TPP catalyst. 2,3-Bis(1-methylpyridinio)norbornadienes were also prepared by a Diels–Alder reaction of bis(1-methylpyridinio)acetylenes with cyclopentadiene. Irradiation of 1-methyl-2-pyridinio and 1-methyl-3-pyridinio derivatives led to the photostationary state between them and the corresponding quadricyclanes, while a 1-methyl-4-pyridinio derivative gave a water or methanol adduct in the presence of water or methanol. Electron-transfer reactions of bis(1-methylpyridinio)norbornadienes were investigated by cyclic voltammetry. The radical cations formed by their reduction were unstable compared with those of the corresponding *trans*-bis(1-methylpyridinio)ethylenes. Steric factors were shown to strongly affect the reactivities.

Valence isomerization between norbornadienes and quadricyclanes has attracted considerable attention from the viewpoint of the reaction mechanism[1] as well as solar energy storage.[2] Since norbornadiene, itself, does not have absorptions above 300 nm, many derivatives have been prepared to extend the absorptions to longer wavelengths.[2] 2,3-Dicyano-1,5,6-trimethyl derivative **1** is a typical compound which shows absorption extending to 400 nm, due to an intramolecular charge-transfer interaction between the dicyanoethylene and dimethylethylene parts.[2c] The mechanism for the photochemical cyclization to give the corresponding quadricyclane was investigated in detail and the high quantum yield could be attributed to the excited state having a charge-transfer property.[3] *In this connection, 2,3-dipyridyl derivatives* **2** are of interest since they can be easily led to the quaternary salts **3** in which the intramolecular interaction resulting in the shifts of absorptions to longer wavelengths is possible. The photochemistry of **2** and **3**, which contain a cis-fixed dipyridylethylene moiety, is intriguing for comparisons with that of dipyridylethylenes in which a cis–trans isomerization occurs.[4] The redox reactions of bis(1-methylpyridinio) derivatives **3** are also interesting since they have a Weitz-type redox system,[5] which is regarded as a viologen analogue. The particularly interesting point is that the bis(1-methylpyridinio)ethylene part is cis-fixed and cannot undergo cis–trans isomerization. The C_5–C_6 double bond may affect the redox reactions. From these viewpoints, we have prepared dipyridylnorbornadienes and investigated their properties.[6]



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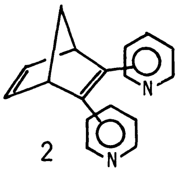

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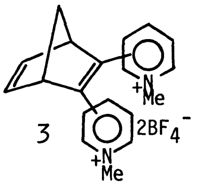
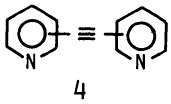


3

a; 4-pyridyl
b; 3-pyridyl
c; 2-pyridyl



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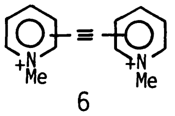
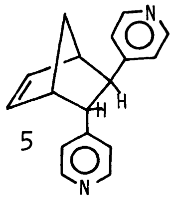


6

a; 4-pyridyl
b; 3-pyridyl
c; 2-pyridyl



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Results and Discussion

Preparation of Dipyridylnorbornadienes. 2,3-Dipyridylnorbornadienes (**2**) were considered to be prepared by a Diels–Alder reaction of dipyridylacetylenes with cyclopentadiene. However, dipyridylacetylenes are weak dienophiles and the reported examples only involve reactions of the 2-pyridyl derivative with tetraphenylcyclopentadienone[7] and coumarin,[8] which require severe conditions. In fact, dipyridylacetylenes

4a—**c**[9] did not undergo a Diels-Alder reaction with cyclopentadiene at all. Therefore, we tried the reaction of the HBF_4 salts of **4a**—**c**, which are considered to be stronger dienophiles due to the more electron-withdrawing property of the pyridinium substituents lowering the LUMO level of the acetylene moiety. The reaction of the HBF_4 salts of **4a**—**c** with cyclopentadiene followed by a treatment with an aqueous sodium hydrogencarbonate solution gave 2,3-dipyridylnorbornadienes **2a**—**c**. The reactivity of the conjugated acid of **4** as a dienophile for the Diels-Alder reaction was dependent on the position of the nitrogen atom in the pyridyl substituents, as can be seen in the reaction conditions listed in Table 1. 2-Pyridyl derivative is the most reactive, while a reaction of the 3-pyridyl derivative requires severe conditions and the yield is poor. The poor reactivity of 3-pyridyl derivative can be explained by considering that the positive charge on the nitrogen atom cannot be delocalized to the acetylenic bond at the meta position. Similarly, the reactivity of *trans*-dipyridylethylene as a dienophile in the Diels-Alder reaction could be enhanced by protonation. Thus, *trans*-di-4-pyridylethylene was recovered upon heating with cyclopentadiene under toluene reflux for 24 h; however, the HBF_4 salt gave *trans*-5,6-di-4-pyridylnorbornene (**5**) in 90% yield upon heating with cyclopentadiene under acetonitrile reflux for 24 h followed by neutralization.

Bis(1-methylpyridinio)acetylenes (**6**) were prepared by the reaction of **4** with trimethyloxonium tetrafluoroborate in good yields. The reaction of **6** with cyclopentadiene under the conditions shown in Table 1 gave 2,3-bis(1-methylpyridinio)norbornadienes (**3**).

Properties of Dipyridylnorbornadienes. The electronic spectra of dipyridylnorbornadienes **2a**—**c** are shown in Fig. 1. All of the norbornadienes **2a**—**c** have end-absorptions around 380 nm, indicating that the introduction of the pyridyl groups shifts the absorption maxima to longer wavelengths. The absorptions are red-shifted in the acidic medium relative to those in a neutral solvent. The 4-pyridyl derivative **2a** has an absorption maximum at 360 nm in an acidic medium. The spectrum of the 2-pyridyl derivative is pH dependent (as shown in Fig. 1), but those of **2a** and **2b** are not. The pH dependence may be attributed to the fact that the conjugated acid has two separate pK_a values, which were determined to be 1.1 and 7.2 by an absorptiometric method. This behavior can be explained by considering that the two pyridyl groups interpose a proton, as shown in the structure **7**,[10] since the absorption of the monoprotonated species is red-shifted compared with that of the di-protonated species; such separate pK_a values are observed in chelate reagents such as 2,2′-bipyridyl and 1,10-phenanthroline. The spectra of 1-methylpyridinium derivatives **3a**,**b**, shown in Fig. 2, are similar to those of the corresponding protonated species. The red shifts caused by quaternarization indicate the presence of a charge-transfer interaction between two olefinic parts. This is also supported by the fact that the absorption of **3a** is red-shifted compared with the corresponding norbornene **8**. On

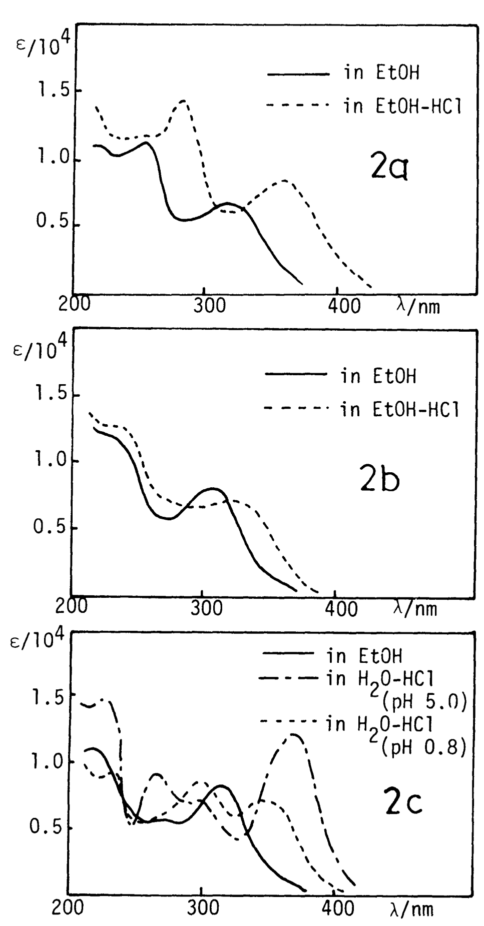


Fig. 1. Electronic spectra of 2,3-dipyridylnorbornadienes (**2**).

Table 1. Diels-Alder Reactions of Dipyridylacetylenes with Cyclopentadiene

Compound	Condition	Product	Yield[a]/%
4a-$(HBF_4)_2$	MeCN reflux 8 h	**2a**	85[b]
4b-$(HBF_4)_2$	MeCN 150 °C 2 d	**2b**	15[b]
4c-$(HBF_4)_2$	MeCN 50 °C 30 min	**2c**	60[b]
6a	MeCN reflux 12 h	**3a**	80
6b	MeCN reflux 2 d	**3b**	30
6c	MeCN 50 °C 10 h	**3c**	80

a) Isolated yield. b) Obtained after treatment with aq $NaHCO_3$.

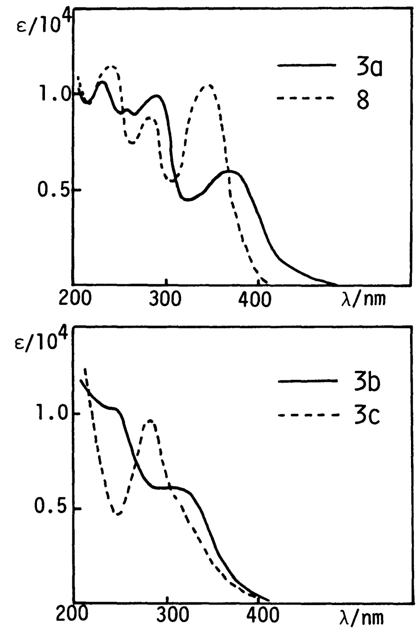
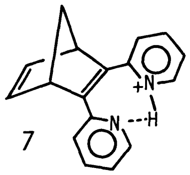


Fig. 2. Electronic spectra of 2,3-bis(1-methylpyridinio)norbornadienes (**3**) and norbornene (**8**).

the other hand, the absorption maximum of **3c** is rather blue-shifted compared with that of the neutral species **2c**. This fact may be attributed to the twisting structure of the 1-methylpyridinium derivative, resulting in a loss of the conjugation of the pyridinium groups with the double bond.



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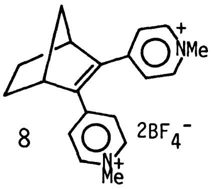
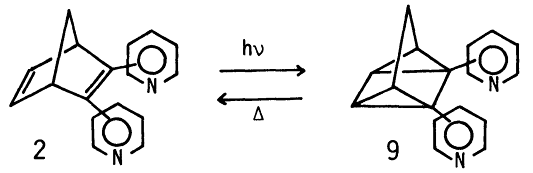
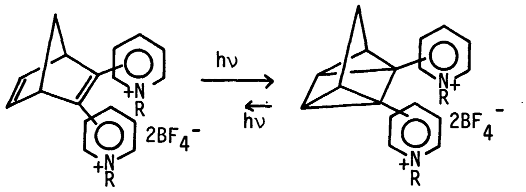


8

Pyridine derivatives, such as 2,2′-bipyridyl, are well-known to be good ligands for metal ions and to form complexes. In the presence of CuCl or $FeSO_4$, red shifts of the absorptions of 4- and 2-pyridyl derivatives **2a** and **2c** were observed, indicating that coordination occurs. On the other hand, the spectrum of 3-pyridyl derivative **2b** was not changed by the addition of CuCl or $FeSO_4$. The reason for no coordination in **2b** is still ambiguous.

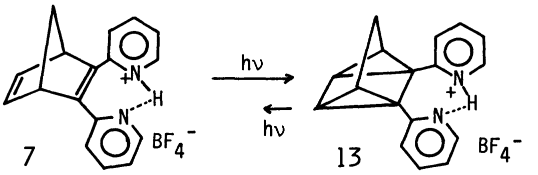


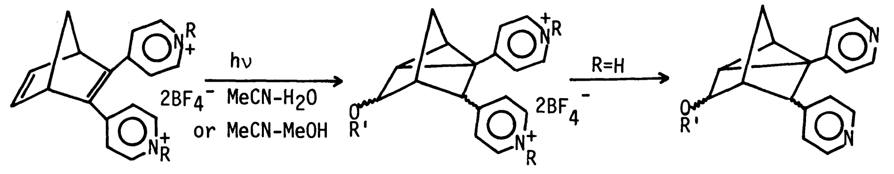
a; 4-pyridyl
b; 3-pyridyl
c; 2-pyridyl



3b; 3-pyridinio, R=Me
3c; 2-pyridinio, R=Me
11b; 3-pyridinio, R=H

10b; 3-pyridinio, R=Me
10c; 2-pyridinio, R=Me
12b; 3-pyridinio, R=H





3a; R=Me
11a; R=H

14a; R=Me, R'=H
14b; R=R'=Me
14c; R=R'=H
14d; R=H, R'=Me

15a; R'=H
15b; R'=Me

Valence Isomerization Reaction. Irradiation of an acetonitrile solution of **2a—c** with Rayonet RUL-3000 Å lamps gave quadricyclanes **9a—c** quantitatively. The quantum yields in acetonitrile were very high and insensitive to the substituents (**2a**; ϕ 0.72, **2b**; ϕ 0.78, **2c**; ϕ 0.79). The yields in cyclohexane were nearly equal (**2a**; ϕ 0.72, **2b**; ϕ 0.71). The photoreaction was affected neither by triplet quenchers, such as 2,5-dimethyl-2,4-hexadiene, 1,3-cyclohexadiene, and oxygen, nor by biacetyl which sensitizes the cis–trans isomerization of dipyridylethylenes. This fact suggests that the reaction proceeds via a singlet state. This is consistent with the fact that the intersystem crossing in dipyridylethylenes is inefficient.11) The photoisomerization of **2a** also proceeded in a solid state quantitatively when a KBr pellet of **2a** was irradiated with a 300-W xenon lamp.

Irradiation of the dimethyl derivatives **3b, c** with Rayonet RUL- 3500 Å lamps led to a photostationary state between **3b, c** and quadricyclanes **10b, c** (**3b**:**10b**=1:4, **3c**:**10c**=2:5). This can be explained by the fact that the resulting quadricyclanes **10b, c** have end-absorptions around 350 nm and undergo cycloreversion under the irradiation conditions. A similar photostationary state was observed upon irradiating a diprotonated derivative **11b** with RUL-3500 Å lamps (**11b**: quadricyclane **12b**=3:7). The irradiation of a monoprotonated derivative **7** with RUL-3000 Å lamps led to a photostationary state between **7** and quadricyclane **13** (**7**:**13**=1:4). However, irradiation with RUL-3500 Å lamps gave **13** quantitatively. This wavelength dependence is explicable by the fact that quadricyclane **13** has no absorption around 350 nm and is stable under the irradiation conditions with 3500 Å lamps. In contrast, irradiation of 4-pyridyl derivative **3a** with RUL-3500 Å lamps in acetonitrile gave a complex mixture of products. Irradiation in the presence of a small amount of water or methanol led to the formation of a water adduct **14a** or a methanol adduct **14b**, respectively.12) In the case of diprotonated derivative **11a**, **15a** or **15b** was isolated after neutralization.12) A treatment of quadricyclane **9a** with HBF_4 in acetonitrile containing methanol followed by neutralization gave **15b**. This result suggests that adducts **14** are formed by a nucleophilic attack of water or methanol on the initially formed quadricyclanes.

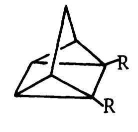
Quadricyclanes **9a—c** underwent a cycloreversion reaction to give norbornadienes **2a—c** upon heating. The activation parameters were calculated (Table 2) from the first-order rate constants determined by a UV spectroscopic method in ethanol. Those values indicate that the introduction of the two pyridyl groups significantly lowers the activation energy compared with that of dicyano13) and bis(methoxycarbonyl) substituents.14) The position of nitrogen of pyridyl substituents has little effect on the reactivities. The salts **10b, c**, **12b**, and **13** also underwent a cycloreversion reaction upon heating at 60 °C in acetonitrile.

Transition metals are well-known to catalyze the cycloreversion reaction of quadricyclanes to norbornadienes.15) However, $Mo(CO)_6$, $Fe_2(CO)_9$, Rh/C, $RhCl(PPh_3)_3$, $Pd(PPh_3)_2Cl_2$, and Fe-TPP (tetraphenylporphyrin) were ineffective for the cycloreversion of quadricyclanes **9a—c** to norbornadienes **2a—c**. Only Co(II)–TPP catalyzed the reaction. The activity of Co(II)–TPP may be attributed to a radicophilic attack of the metal to the electronegative substituted quadricyclanes, as reported by Yoshida et al.16) On the other hand, Co(II)–TPP did not catalyze the cycloreversion of dications **10b, c** and **12b** although it catalyzed that of monocation **13**. This fact may be caused by a Coulomb repulsion which makes it difficult for the catalyst to approach the dications.

Electron-Transfer Reactions of 2,3-Bis(1-methylpyridinio)norbornadienes (3). Norbornadienes **3** possess a Weitz-type redox system,5) as shown in Scheme 1. The electron-transfer reactions of **3**, which have a cis-fixed bis(1-methylpyridinio)ethylene skeleton, are of particular interest since bis(1-methylpyridinio)ethylenes usually undergo cis–trans isomerization upon reduction.17) The reduction potentials of **3a—c** and norbornene **8** measured by cyclic voltammetry (c.v.) are summarized in Table 3. The waves for **3a**, **3c**, and **8** are reversible or quasi-reversible for the following reasons. The current ratios, i_{pa}/i_{pc}, were near unity. They and the half-wave reduction potentials, $E_{1/2}^{red}$, were independent on the scan rates, v. The cathodic peak current, i_{pc}, was proportional to $v^{1/2}$. In contrast, the wave for **3b** was irreversible. Since the i_{pc} was proportional to $v^{1/2}$, the irreversible property can be attributed to the lability of a product formed by the reduction on the c.v. time scale. This seems to be

Table 2. Activation Parameters for Cycloreversion of Quadricyclanes

R	E_a/kJ mol^{-1}	log A	ΔS/J K^{-1} a)
4-pyridyl (**9a**)	115.1	13.0	−5.3
3-pyridyl (**9b**)	113.0	12.7	−11.0
2-pyridyl (**9c**)	116.3	13.2	−1.4
H b)	160.2	15.0	—
CO_2Me b)	146.0	14.3	—
CN c)	141.4	7.5	—

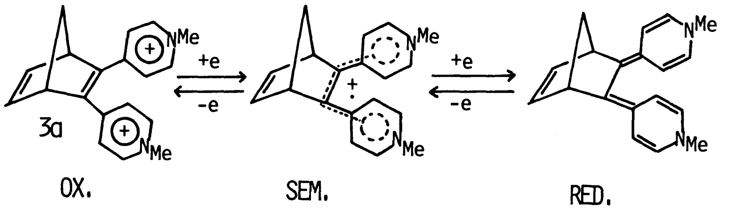


a) At 60 °C. b) In toluene.14) c) In acetonitrile.13)

Table 3. Data for the Cyclic Voltammetry[a]

Compound	Solvent	$E^{red}_{1/2}$/V vs. SCE	$E_{p/2}$/V	(E_1-E_2/V[b])	log K_{sem}[c]
3a	DMF	−0.59	0.061	0.04	0.68
	MeCN	−0.67	0.079	0.08	1.4
	CH_2Cl_2	−0.43, −0.52	—	0.095[d]	1.6
3b	DMF	−1.05[e]	—	—	—
	MeCN	−1.12[e]	—	—	—
	CH_2Cl_2	−0.90[e]	—	—	—
3c	DMF	−0.70	0.050	0.02	0.34
	MeCN	−0.78	0.040	0	0
	CH_2Cl_2	−0.57	0.040	0	0
8	MeCN	−0.74	0.085	0.085	1.4
	CH_2Cl_2	−0.50, −0.60	—	0.10[d]	1.7

a) 0.1 mol dm^{-3} Et_4NClO_4 in MeCN or DMF, or 0.1 mol dm^{-3} Bu_4NBF_4 in CH_2Cl_2, Pt electrode, scan rate 100 mV s^{-1}. b) Analyzed by Myers and Shain's method.[19] c) log $K_{sem}=(E_1-E_2)/0.059$. d) Observed value. e) Irreversible.



Scheme 1.

related to the nature of the meta-derivative in which the cation or radical cannot conjugate with the double bond.

Since norbornadiene **3a** has the same electron-accepting part as norbornene **8**, the differences in the behavior of the electron-transfer reactions are considered to reflect the difference in the structures. Both of their c.v. revealed only one wave in *N,N*-dimethylformamide (DMF) and acetonitrile. However, the peak widths, $\Delta E_{p/2}$, are different from that for the usual one-electron transfer (56.5 mV), suggesting that a one-electron transfer occurs closely in two stages. In fact, the separated potentials were observed in dichloromethane. The cation radical species are more stabilized in dichloromethane than in acetonitrile.[18] The differences between the first and second reduction potentials (E_1-E_2) were calculated according to the Myers and Shain's method,[19] as shown in Table 3. The semiquinone formation constants, K_{sem}, calculated as log $K_{sem}=(E_1-E_2)/0.058$ are also shown in Table 3. Those values are much smaller than that of *trans*-bis(1-methylpyridinio)ethylenes whose pyridinio groups are coplanar.[20] The first reduction potential of **3a** is a little higher than that of **8**. This may be caused by the interaction between the two olefinic parts, which lowers the LUMO level of the bis(1-methylpyridinio)ethylene moiety.

On the other hand, the c.v. of 2-pyridinio derivative **3c** revealed one peak with small values of $\Delta E_{p/2}$ even in dichloromethane. The (E_1-E_2) values determined by Myers and Shain's method are zero or nearly zero as shown in Table 3. This fact shows that a one-electron transfer occurs very closely in two stages or a two-electron transfer occurs in one stage. The reason for this may be attributed to a steric effect for the 1-methyl groups, decreasing the conjugation between the 2-pyridinio groups and the double bond.

The radical cations of **3a** and **8**, generated electrochemically in degassed acetonitrile containing 0.1 mol dm^{-3} of tetraethylammonium perchlorate, were observed in the ESR spectrum. The *g*-values were both 2.0025, which were determined using 2,2-diphenyl-1-picrylhydrazyl as a standard. Interestingly, the lifetime for the radical cation of **3a** ($t_{1/2}$=104 s at 20 °C) was longer than that for the radical cation of **8** ($t_{1/2}$=36 s at 18 °C). The decay of the former obeyed second-order kinetics, indicating disproportionation, while that of the latter was first-order, indicating a reaction with a substance such as the solvent or the electrolyte. This result shows that the nonconjugated double bond decreased the reactivity of the radical cation species.

Experimental

Electronic spectra were obtained on a Hitachi 340 spectrophotometer. IR spectra were taken on a Shimadzu IR-27G spectrometer. Mass data were collected on a Hitachi M-52 mass spectrometer. ^1H and ^{13}C NMR spectra were obtained at 90 MHz on a Varian EM-390 and at 50 MHz on a Varian XL-200 spectrometer, respectively. Redox potentials were measured on a Yanako p-1000 voltammetric analyzer. Dichloromethane and acetonitrile were distilled from calcium hydride. Melting points are uncorrected.

HBF_4 Salts of Dipyridylacetylenes (4). To a solution of

200 mg (1.1 mmol) of di-4-pyridylacetylene (**4a**) in 200 ml of ether, 1 ml of 42% HBF_4 was added with vigorous stirring. The precipitated colorless solid was collected by filtration and dried to give 370 mg (88%) of the HBF_4 salt of **4a**: mp 260—270 °C (decomp). Found: C, 40.64; H, 2.82; N, 8.10%. Calcd for $C_{14}H_{18}N_2BF_4$: C, 40.51; H, 2.83; N, 7.87%. Similarly, the HBF_4 salts of **4b** and **4c** were obtained as colorless solids. **4b**-$2HBF_4$: mp 240—270 °C (decomp). Found: C, 40.90; H, 2.88; N, 8.42%. Calcd for $C_{14}H_{18}N_2BF_4$: C, 40.51; H, 2.83; N, 7.87%. **4c**-$2HBF_4$: mp 235—245 °C (decomp). Found: C, 40.00; H, 2.91; N, 8.25%. Calcd for $C_{14}H_{18}N_2BF_4$: C, 40.51; H, 2.83; N, 7.87%.

2,3-Di-4-pyridylbicyclo[2.2.1]hepta-2,5-diene (2a). A solution of 302 mg (0.85 mmol) of the HBF_4 salt of **4a** and 1.1 ml of cyclopentadiene in 30 ml of dry acetonitrile was refluxed for 8 h. After the solvent was removed, 50 ml of water containing a small amount of HBF_4 was added and the mixture was extracted with dichloromethane (3×30 ml). The aqueous layer was neutralized with $NaHCO_3$ and extracted with dichloromethane (4×30 ml). The organic extract was dried over Na_2SO_4 and the solvent was removed to give 178 mg (85%) of **2a**, which was recrystallized from hexane to give **2a** as colorless needles: mp 110—111 °C; IR (KBr) 1620, 1591, 1551, 1529, 1492, 1443, 1408, 1391, 1210, 1068, 1050, 978, 943, 872, 850, 800, 718 cm^{-1}; UV (EtOH) 243 nm (log ε 4.06), 315 (3.83); MS (25 eV) m/z (relative intensity) 246 (M^+, 100%), 181 (78%); ^1H NMR ($CDCl_3$, 90 MHz) δ=2.15 (dt, 1H, J=6.3, 3.0 Hz), 2.39 (dt, 1H, J=6.3, 3.0 Hz), 3.92 (m, 2H), 6.99 (m, 6H), 8.43 (m, 4H); ^{13}C NMR ($CDCl_3$) δ=57.23, 71.45, 121.95, 143.15, 144.75, 150.60, 151.26. Anal. ($C_{17}H_{14}N_2$) C, H, N.

2,3-Di-3-pyridylbicyclo[2.2.1]hepta-2,5-diene (2b). A mixture of 318 mg (0.83 mmol) of the HBF_4 salt of **4b** and 3 ml of cyclopentadiene in 15 ml of argon-purged dry acetonitrile was sealed in a Pyrex tube. Heating at 160 °C for 3 d and similar workup as for **2a** gave a yellow oil, which was separated by thin-layer chromatography on alumina (4:1 dichloromethane–ether) to give 32 mg (16%) of **2b**. Recrystallization from hexane gave **2b** as colorless leaflets: mp 100—101 °C; IR (KBr) 3040, 2980, 2950, 1565, 1483, 1405, 1284, 1012, 722, 680 cm^{-1}; UV (MeCN) 231 nm (log ε 4.08), 252 (3.96), 306 (3.92); MS (25 eV) m/z (relative intensity) 246 (M^+, 58), 181 (100), 180 (81); ^1H NMR ($CDCl_3$) δ=2.13 (dm, 1H, J=6.0 Hz), 2.42 (dm, 1H, J=6.0 Hz), 3.90 (m, 2H), 6.95 (m, 2H), 7.30 (dd, 2H, J=7,5, 4.5 Hz), 7.85 (dm, 2H, J=7.5 Hz), 8.2—8.6 (m, 4H). Anal. ($C_{17}H_{14}N_2$) C, H, N.

2,3-Di-2-pyridylbicyclo[2.2.1]hepta-2,5-diene (2c). A solution of 596 mg (1.56 mmol) of the HBF_4 salt of **4c** and 1 ml of cyclopentadiene in 80 ml of dry acetonitrile was heated under nitrogen at 50 °C for 30 min. A similar workup as that for **2a** gave 224 mg (54%) of **2c**, which was recrystallized from hexane to give colorless needles: mp 72—73 °C; IR (KBr) 1582, 1576, 1452, 1428, 1419, 1282, 1269, 771, 761, 730, 713, 676, 668 cm^{-1}; UV (EtOH) 223 nm (log ε 4.06), 316 (3.93); MS (25 eV) m/z (relative intensity) 245 (M^+, 100), 181 (34), 168 (73); ^1H NMR ($CDCl_3$) δ=2.10 (dt, 1H, J=6.2, 3.0 Hz), 2.42 (dt, 1H, J=6.2, 3.0 Hz), 4.20 (m, 2H), 7.18 (m, 8H), 8.55 (m, 2H). Anal. ($C_{17}H_{14}N_2$) C, H, N.

***trans*-5,6-Di-4-pyridylbicyclo[2.2.1]hept-2-ene (5).** A solution of 150 mg (0.42 mmol) of the HBF_4 salt of *trans*-1,2-di-4-pyridylethylene and 2 ml of cyclopentadiene in 100 ml of dry acetonitrile was heated under reflux for 24 h. A similar workup as that for **2a** gave 94 mg (90%) of **5** as colorless needles: mp 92—94 °C (from hexane); IR (KBr) 3000, 1600, 1553, 1412, 1335, 985, 845, 830, 795, 770, 725, 640, 590 cm^{-1}; MS (25 eV) m/z (relative intensity) 248 (M^+, 14), 183 (100), 180 (50).

Bis(1-methylpyridinio)acetylenes (6a—c). A mixture of 2.1 g (14 mmol) of trimethyloxonium tetrafluoroborate and 500 mg of di-4-pyridylacetylene (**4a**) in 18 ml of nitromethane was stirred under nitrogen at r.t. for 2 d. After 2 ml of methanol was added, the mixture was stirred for an additional 2 h and poured into 300 ml of ether with vigorous stirring to give 1.06 g (100%) of **6a**. Recrystallization from acetonitrile–dichloromethane–ether gave **6a** as colorless needles: mp 270—280 °C (decomp). Anal. ($C_{14}H_{14}N_2B_2F_8$) C, H, N. In a similar manner, 3-pyridyl derivative **6b** and 2-pyridyl derivative **6c** were prepared. **6b**: mp 255—265 °C (decomp). Anal. ($C_{14}H_{14}N_2B_2F_8$) C, H, N. **6c**: mp 260—268 °C (decomp). Anal. ($C_{14}H_{14}N_2B_2F_8$) C, H, N.

2,3-Bis(1-methyl-4-pyridinio)bicyclo[2.2.1]hepta-2,5-diene Bis(tetrafluoroborate) (3a). A solution of 165 mg (0.42 mmol) of acetylene **6a** and 1.5 ml of cyclopentadiene in 20 ml of dry acetonitrile was heated during reflux under nitrogen for 12 h. The cooled mixture was poured into 200 ml of ether to give 152 mg (90%) of **3a**: mp 220—225 °C (decomp) (from acetonitrile–ether); IR (KBr) 3050, 1640, 1560, 1520, 1470, 1285, 1050, 840, 730, 530, 515 cm^{-1}; UV (MeCN) 223 nm (log ε 4.03), 255 (3.98), 286 (4.00), 364 (3.80); ^1H NMR (CD_3CN) δ=2.23 (dm, 1H, J=7.5 Hz), 2.57 (dm, 1H, J=7.5 Hz), 4.20 (m, 2H), 4.35 (s, 6H), 7.08 (t, 2H, J=1.5 Hz), 7.68 (d, 4H, J=6.0 Hz), 8.45 (d, 4H, J=6.0 Hz). ^{13}C NMR (CD_3CN) δ=46.68, 58.58, 72.66, 126.48, 143.68, 146.41, 152.27, 156.32. Anal. ($C_{19}H_{20}N_2B_2F_8$) C, H, N.

2,3-Bis(1-methyl-3-pyridinio)bicyclo[2.2.1]hepta-2,5-diene Bis(tetrafluoroborate) (3b). A solution of 184 mg (0.48 mmol) of acetylene **6b** and 2 ml of cyclopentadiene in 20 ml of dry acetonitrile was heated during reflux under nitrogen for 2 d. A similar work-up as that for **3a** gave 32 mg of **3b**: mp 180—185 °C (decomp) (from acetonitrile–ether); IR (KBr) 3300, 1630, 1552, 1468, 1280, 1250, 1050, 795, 670, 515 cm^{-1}; UV (MeCN) 245 nm (log ε 4.03), 280 sh (3.84), 314 (3.79); ^1H NMR (CD_3CN) δ=2.20 (dm, 1H, J=6.0 Hz), 2.55 (dm, 1H, J=6.0 Hz), 4.05 (tm, 2H, J=1.5 Hz), 4.25 (s, 6H), 7.10 (tm, 2H, J=1.5 Hz), 7.85 (dm, 2H, J=7.5 Hz), 8.20 (dm, 2H, J=7.5 Hz), 8.45—8.60 (m, 4H). Anal. ($C_{19}H_{20}N_2B_2F_8$) C, H, N.

2,3-Bis(1-methyl-2-pyridinio)bicyclo[2.2.1]hepta-2,5-diene Bis(tetrafluoroborate) (3c). A solution of 130 mg (0.36 mmol) of acetylene **6c** and 2 ml of cyclopentadiene in 15 ml of dry acetonitrile was heated under nitrogen at 50 °C for 10 h. A similar workup as that for **3a** gave 119 mg (74%) of **3c**: mp 235—255 °C (decomp) (acetonitrile–ether); IR (KBr) 3100, 1625, 1580, 1510, 1455, 1265, 1050, 778, 762, 735, 720, 512 cm^{-1}; UV (MeCN) 284 nm (log ε 3.99), 328 (3.64); ^1H NMR (CD_3CN) δ=2.35 (dm, 1H, J=7.0 Hz), 2.80 (dm, 1H, J=7.0 Hz), 4.10 (s, 6H), 4.30 (tm, 2H, J=1.5 Hz), 7.10 (t, 2H, J=1.5 Hz), 7.52 (dm, 2H, J=8.0 Hz), 7.85 (ddm, 2H, J=8.0, 6.0 Hz), 8.25 (tm, 2H, J=8.0 Hz), 8.65 (dm, 2H, J=6.0 Hz). Anal. ($C_{19}H_{20}N_2B_2F_8$) C, H, N.

2,3-Di-4-pyridylbicyclo[2.2.1]hept-2-ene. In a hydrogenation apparatus, 202 mg (0.82 mmol) of norbornadiene **2a** was hydrogenated in 22 ml of ethyl acetate with 5 ml of 5% Pd–C. Removal of the catalyst and solvent followed by recrystallization from hexane gave 115 mg (57%) of a norbornene derivative as colorless needles: mp 121—123 °C;

IR (KBr) 3075, 2980, 2870, 1592, 1538, 1414, 1271, 1115, 810, 760, 588, 518 cm^{-1}; UV (MeCN) 227 (log ε 4.06), 239 (3.97), 288 (3.98); MS (25 eV) *m/z* (relative intensity) 248 (M$^+$, 46%), 220 (100%); ^{1}H NMR (CDCl$_3$) δ=1.2—1.4 (m, 3H), 1.6—2.1 (m, 5H), 3.30 (brs, 2H), 7.05 (dm, 4H, *J*=6.0 Hz), 8.46 (dm, 4H, *J*=6.0 Hz); ^{13}C NMR (CDCl$_3$) δ=26.40, 47.90, 49.55, 123.14, 144.17, 144.64, 150.89. Anal. ($C_{17}H_{16}N_2$) C, H, N.

2,3-Bis(1-methyl-4-pyridinio)bicyclo[2.2.1]hept-2-ene Bis(tetrafluoroborate) (8). A solution of 76 mg (0.31 mmol) of 2,3-di-4-pyridylnorbornene and 250 mg (1.68 mmol) of trimethyloxonium tetrafluoroborate in 8 ml of nitromethane was stirred at room temperature for 2 d. After 1 ml of methanol was added, the mixture was stirred for 1 h, concentrated to 4 ml, and then poured into 80 ml of ether with vigorous stirring. The resulting crystals were filtered and washed with cold acetone to give 74 mg (53%) of **8** as colorless needles: mp 220—225 °C, IR (KBr) 2950, 1640, 1520, 1470, 1270, 1050, 832, 513 cm^{-1}; UV (MeCN) 238 nm (log ε 4.08), 280 (3.96), 341 (4.04); ^{1}H NMR (CD$_3$CN) δ=1.35—1.6 (m, 4H), 1.8—2.2 (m, 2H), 3.50 (m, 2H), 4.26 (s, 6H), 7.70 (d, 4H, *J*=7.5 Hz), 8.47 (d, 4H, *J*=7.5 Hz). ^{13}C NMR (CD$_3$CN) δ=25.91, 48.58, 48.68, 50.43, 127.28, 146.31, 147.94, 151.99. Anal. ($C_{19}H_{22}N_2B_2F_8$) C, H, N.

1,5-Di-4-pyridyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane (9a). A solution of 102 mg (0.61 mmol) of norbornadiene **2a** in 70 ml of acetonitrile was irradiated through a Pyrex filter with Rayonet RUL-3000 Å lamps under nitrogen bubbling for 1 h. Removal of the solvent followed by recrystallization from pentane gave 86 mg (84%) of **9a** as colorless needles: mp 92.5—93 °C; IR (KBr) 1588, 1531, 1491, 1405, 1200, 1141, 972, 797, 780, 761, 502 cm^{-1}; UV (EtOH) 261 nm (log ε 3.99); MS (25 eV) *m/z* (relative intensity) 246 (M$^+$, 100), 181 (97), 66 (93); ^{1}H NMR (CCl$_4$) δ=2.00 (m, 2H), 2.38 (m, 4H), 6.72 (m, 4H), 8.24 (m, 4H). Anal. ($C_{17}H_{14}N_2$) C, H, N.

In a similar manner, 3-pyridyl derivative **9b** and 2-pyridyl derivative **9c** were obtained in 80—90% yields. **9b**: mp 95—98 °C; IR (KBr) 3050, 1570, 1482, 1420, 1150, 1010, 822, 798, 708, 617 cm^{-1}; UV (MeCN) 246 nm (log ε 3.89), 270 (3.79); MS (25 eV) *m/z* (relative intensity) 246 (M$^+$, 58), 181 (100), 180 (81); ^{1}H NMR (CDCl$_3$) 1.95 (dm, 2H, *J*=4.5 Hz), 2.28 (dm, 1H, *J*=12.0 Hz), 2.33 (d, 2H, *J*=4.5 Hz), 2.48 (dm, 1H, *J*=12.0 Hz), 7.07 (ddm, 2H, *J*=7.5, 4.5 Hz), 7.27 (dt, 2H, *J*=7.5 Hz), 8.2—8.5 (m, 4H). Anal. ($C_{17}H_{14}N_2$) C, H, N. **9c**: mp 61—62 °C; IR (KBr) 1582, 1558, 1468, 1428, 819, 769, 751, 738 cm^{-1}; UV (EtOH) 239 nm (log ε 3.92), 273 (3.85); MS (25 eV) *m/z* (relative intensity) 246 (M$^+$, 93), 181 (44), 168 (100); ^{1}H NMR (CDCl$_3$) δ=2.20 (m, 3H), 2.50 (m, 3H), 6.93 (m, 4H), 7.35 (m, 2H), 8.37 (m, 2H). Anal. ($C_{17}H_{14}N_2$) C, H, N.

Irradiation of the HBF$_4$ Salt 7. A solution of 30 mg (0.090 mmol) of **7** in nitrogen-purged acetonitrile was irradiated with Rayonet RUL-3500 Å lamps for 30 min. Removal of the solvent gave quadricyclane **13** as yellow needles quantitatively: mp 245—250 °C (decomp); IR (KBr) 1610, 1590, 1480, 1432, 890, 778, 765, 585, 515 cm^{-1}; ^{1}H NMR (CD$_3$CN) δ=2.37 (dm, 1H, *J*=6.0 Hz), 2.58 (d, 2H, *J*=4.0 Hz), 2.60 (dm, 1H, *J*=6.0 Hz), 2.94 (d, 2H, *J*=4.0 Hz), 7.05 (dm, 2H, *J*=9.0 Hz), 7.43 (tm, 2H, *J*=7.5 Hz), 7.97 (ddm, 2H, *J*=9.0, 7.5 Hz), 8.63 (dm, 2H, *J*=6.0 Hz). Anal. ($C_{17}H_{15}N_2BF_4$) C, H, N.

Irradiation of Dimethyl Derivatives 3b, c. A solution of 30 mg (0.067 mmol) of **3b** in 5 ml of argon-purged acetonitrile was irradiated with Rayonet RUL-3500 Å lamps for 1 h. Removal of the solvent gave a mixture of **3b** and quadricyclane **10b** whose ^{1}H NMR spectrum showed the ratio of **3b** and **10b** to be 1 : 4. The ratio was not changed by prolonged irradiation. Similarly, irradiation of **3c** with Rayonet RUL-3500 Å lamps gave a mixture of **3c** and **10c** whose ratio was 2 : 5 from the ^{1}H NMR spectrum.

Irradiation of Dimethyl Derivative 3a. A solution of 30 mg (0.067 mmol) of **3a** in argon-purged acetonitrile–methanol (3 : 1) was irradiated through a Pyrex filter with Rayonet 3500 Å lamps for 1 h. Removal of the solvent gave a yellow solid of **14b** whose structure was deduced from the ^{1}H NMR spectrum: (CD$_3$CN) δ=1.8—2.3 (m, 5H), 2.7—2.9 (m, 1H), 3.19 (s, 2.2H), 3.34 (s, 0.8H), 3.8—4.0 (m, 1H), 4.14 (s, 3H), 4.27 (s, 3H), 7.46 (d, 2H, *J*=6.0 Hz), 7.71 (d, 2H, *J*=6.0 Hz), 8.33 (d, 2H, *J*=6.0 Hz), 8.49 (d, 2H, *J*=6.0 Hz).

Irradiation of the HBF$_4$ Salt 11a. A solution of 80 mg (0.19 mmol) of **11a** in 10 ml of nitrogen-purged acetonitrile through a Pyrex filter with Rayonet RUL-3500 Å lamps for 30 min. A mixture obtained after removal of the solvent was dissolved in water, neutralized with NaHCO$_3$, and then extracted with dichloromethane. After the organic extract was dried over Na$_2$SO$_4$, removal of the solvent gave **15a** as a pale yellow oil, whose structure was deduced from the ^{1}H NMR spectrum: (CDCl$_3$) δ=1.5—2.3 (m, 7H), 3.9—4.2 (m, 1H), 6.84 (m, 2H), 7.02 (m, 2H), 8.3—8.5 (m, 4H).

Similarly, irradiation of **11a** in acetonitrile–methanol (3 : 1) gave **15b** as a yellow oil: ^{1}H NMR (CDCl$_3$) δ=1.6—1.9 (m, 2H), 2.0—2.5 (m, 3H), 3.19 (s, 2.2H), 3.34 (s, 0.8H), 3.4—4.9 (m, 2H), 6.79 (dm, 2H, *J*=6.0 Hz), 6.99 (dm, 2H, *J*=6.0 Hz), 8.38 (m, 4H).

Quantum Yield Determinations. Samples were irradiated with an Ushio 150-W xenon lamp on a Hitachi MPF-4 spectrometer (λ_{ex}=334±10 nm). The number of photons incident on the samples were determined by using a potassium trioxalatoferrate(III) actinometer. The reactions were followed by the electronic spectra.

Rate Constant Determinations. Solutions of 0.9—1.3×10^{-4} mol dm^{-3} of quadricyclanes **9a—c** in absolute ethanol were heated in a thermostat (RAUDA-WB20D). The rate constants were determined by an absorptiometric method.

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