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Preparation and Photoreactions of Bispyridylnorbornadienes[1)]

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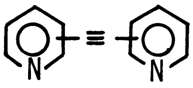
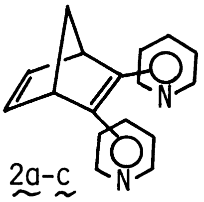
Bispyridylnorbornadienes were synthesized using the Diels-Alder reaction of HBF_4 salts of bispyridylacetylenes with cyclopentadiene. They underwent the photocyclization to give quadricyclanes which reverted to norbornadienes by heating or a catalyst. Bis(N-methylpyridyl)norbornadienes were also synthesized and the photoreactions were investigated.

Recently much attention has been focused on valence isomerization between norbornadienes and quadricyclanes from the viewpoint of the reaction mechanism[2)] as well as the solar energy storage.[3)] Although many norbornadiene derivatives have been prepared to extend the absorption to the longer wavelength,[3)] bispyridyl substituted norbornadienes have not been reported yet. They are expected to show interesting properties due to the bispyridylethylene moiety whose pyridine rings can be converted to the quaternary salts. Their photochemistry is interesting for comparisons with that of bispyridylethylenes which has been extensively studied.[4)] The redox reactions of the quaternary salts are also attractive since they are considered to be viologen analogues.[5)] We report here the preparation and photoreactions of bispyridylnorbornadienes.

Bispyridylacetylenes **1a-c**[6)] did not undergo the Diels-Alder reaction with cyclopentadiene at all. However, the HBF_4 salts of **1a-c** gave bispyridylnorbornadienes **2a-c**[7)] by the reaction with cyclopentadiene followed by treatment with aqueous sodium hydrogencarbonate solution. The rates of the reaction were dependent on the substituents as seen in the reaction conditions shown in Table 1. These findings indicate that the Diels-Alder reaction is facilitated by the electron-withdrawing pyridinium substituents lowering the LUMO level of the acetylene moiety.

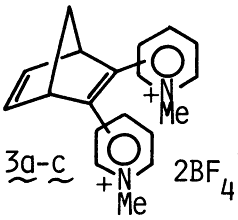


1a-c



2a-c

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



3a-c

Similarly, the Diels-Alder reaction of BF_4^- salts of bis(N-methylpyridyl)-acetylenes[8)] with cyclopentadiene led to the formation of norbornadienes **3a**-**c**[7)] in the yields shown in Table 1. The absorption maxima in the UV spectra of **2a**-**c** and **3a**-**c** are shown in Table 2. For comparison, norbornene derivatives **4** and **5** were synthesized by the catalytic reduction of the corresponding norbornadienes. The absorptions of norbornadienes are red-shifted relative to those of the corresponding norbornenes, suggesting the presence of the interaction between the double bonds in the norbornadiene skeleton. Another interesting feature is that the UV spectrum of **2c** is pH dependent [λmax 368 nm (logε 4.02) in H_2O pH 5.0, 346 nm (logε 3.86) in H_2O pH 0.6]. This is attributed to the fact that **2c** has two sepatate pKa values (pKa_2 7.2, pKa_1 1.1),[9)] which suggests that the monoprotonated form is stabilized by the two pyridyl groups interposing the proton as shown in the structure **6**.

Irradiation of an acetonitrile solution of **2a**-**c** with Rayonet RUL-3000 Å lamps resulted in the quantitative formation of quadricyclanes **7a**-**c**. The quantum yields measured in acetonitrile at room temperature by a potassium ferrioxalate actinometer (λex. 334 ± 10 nm) were very high (**2a**;Φ 0.72, **2b**;Φ 0.78, **2c**;Φ 0.79). The quantum yields were also high in cyclohexane (**2a**;Φ 0.72, **2b**;Φ 0.71). The photoreaction seems to proceed via a singlet state since the reaction was affected neither by triplet quenchers such as 2,5-dimethyl-2,4-hexadiene and 1,3-cyclohexadiene nor by biacetyl which sensitizes the cis-trans isomerization of bispyridylethylenes.

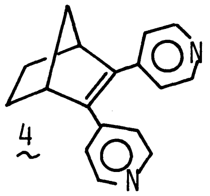
Table 1. Diels-Alder reaction of bispyridylacetylenes with cyclopentadiene

Compound	Conditions	Product		
			Yield[a)]/%	Mp/°C
1a-$(HBF_4)_2$	MeCN reflux 8 h	**2a**[b)]	85	110-111
1b-$(HBF_4)_2$	MeCN 150 °C 2 d	**2b**[b)]	15	100-101
1c-$(HBF_4)_2$	MeCN 50 °C 30 min	**2c**[b)]	60	72-73
1a-$(MeBF_4)_2$	MeCN reflux 12 h	**3a**	80	220-225
1b-$(MeBF_4)_2$	MeCN reflux 2 d	**3b**	30	180-185
1c-$(MeBF_4)_2$	MeCN 50 °C 10 h	**3c**	80	235-255

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

Table 2. Absorption maxima in the UV spectra of norbornadienes **2** and **3**, and norbornenes **4** and **5**

Compound	λmax/nm (logε) in EtOH
2a	243 (4.06) 315 (3.83)
2b	231 (4.08) 252sh (3.96) 306 (3.92)
2c	223 (4.06) 316 (3.93)
3a	233 (4.03) 255 (3.98) 286 (4.00) 364 (3.80)
3b	245 (4.03) 280sh (3.84) 314 (3.79)
3c	284 (3.99) 328sh (3.64)
4	227 (4.06) 239 (3.97) 288 (3.98)
5	238 (4.08) 280 (3.96) 341 (4.04)



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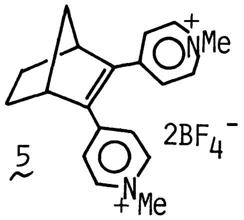

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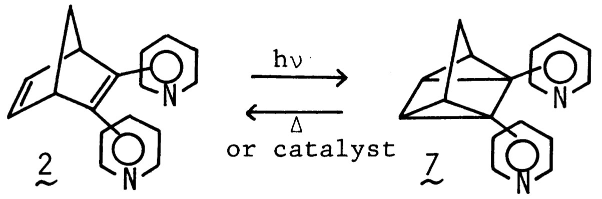
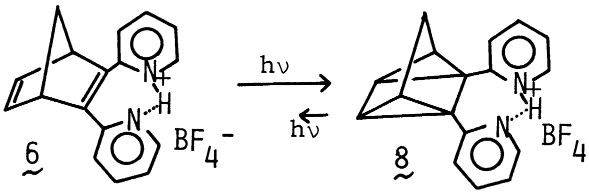
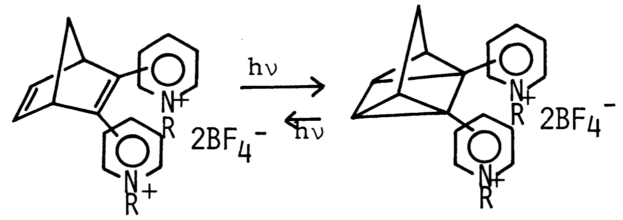
This is consistent with the fact that the intersystem crossing in bispyridylethylenes is inefficient.[10)] Quadricyclanes 7a-c reverted to norbornadienes 2a-c by heating. The following activation parameters at 70 °C in ethanol were obtained from the first order rate constants determined at four different temperatures by a UV spectroscopic method. 7a; ΔH^* 112.2 kJ mol^{-1}, ΔS^* -5.5 J K^{-1} mol^{-1}, 7b; ΔH^* 110.1 kJ mol^{-1}, ΔS^* -11.3 J K^{-1} mol^{-1}, 7c; ΔH^* 113.4 kJ mol^{-1}, ΔS^* -1.7 J K^{-1} mol^{-1}. These values indicate that the introduction of the bispyridyl substituents lowers the activation energy for the cycloreversion compared with that of dicyano[11)] and dicarbomethoxy substituents.[12)] The position of nitrogen of pyridyl substituents has little effect on the rate of reaction. The catalytic cycloreversion was accomplished by cobalt tetraphenylporphyrin at room temperature.

For comparisons with the photoreactions of bispyridylnorbornadienes 2, those of the quaternary salts were investigated. Irradiation of monoprotonated derivative 6 with Rayonet RUL-3500 Å lamps gave quadricyclane 8 quantitatively. However, irradiation with RUL-3000 Å lamps led to the photostationary state between 6 and 8 (6:8 = 19:81).[13)] This wavelength dependent photoreaction can be explained by considering the reverse reaction of quadricyclane 8 to norbornadiene 6 since 8 has end absorptions at 300 nm. The similar photostationary state was observed in the photoreaction of the dimethylated derivatives 3b,c and diprotonated derivative 10b in which the ratios of norbornadienes to quadricyclanes were 30:70, 12:88, and



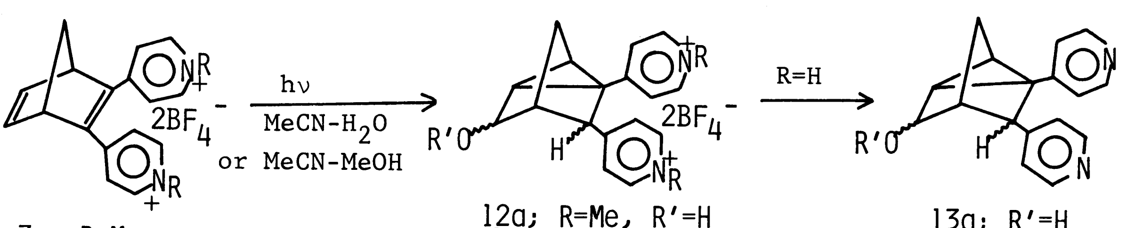
a; 4-pyridyl
b; 3-pyridyl
c; 2-pyridyl





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

9b; 3-pyridyl, R=Me
9c; 2-pyridyl, R=Me
11b; 3-pyridyl, R=H



3a; R=Me
10a; R=H

12a; R=Me, R'=H
12b; R=R'=Me
12c; R=R'=H
12d; R=H, R'=Me

13a; R'=H
13b; R'=Me

30:70, respectively, by irradiation with RUL-3500 Å lamps. In contrast, irradiation of 4-pyridyl derivative **3a** with RUL-3500 Å lamps in acetonitrile containing a small amount of water or methanol gave a water adduct **12a** or a methanol adduct **12b**, respectively.[14)] In the case of diprotonated derivative **10a**, **13a** or **13b** was isolated in high yields after neutralization. **13b** was also isolated by treatment of quadricyclane **7a** with HBF_4 in acetonitrile containing methanol followed by neutralization. This result suggests that **12** are formed by the nucleophilic attack of water or methanol to the initially formed quadricyclanes. The electron-transfer reactions of the dimethylated derivatives **3a**-**c** are currently investigated.

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7) All new compounds obtained here showed satisfactory elemental analyses and spectral data.
8) Bis(N-methylpyridyl)acetylenes were prepared by reaction of the acetylenes with trimethyloxonium tetrafluoroborate.
9) This measurement was carried out by a UV spectroscopic method. The pKa values of **2a** was between 5.5 and 6.5, but the exact values could not be obtained since pKa_1 and pKa_2 are too close. The pKa values of **2b** could not be measured because of small difference in absorbance between neutral and acidic species.
10) D. G. Whitten and M. T. McCall, J. Am. Chem. Soc., 91, 5097 (1969).
11) J. R. Edman, J. Org. Chem., 32, 2920 (1967).
12) D. S. Kabakoff, J-C. G. Bünzli, J. F. M. Oth, W. B. Hammond, and J. A. Berson, J. Am. Chem. Soc., 97, 1510 (1975).
13) The ratio was determined by ^1H NMR.
14) The photoreaction in dry acetonitrile gave a complex mixture of products, suggesting that the initially formed quadricyclanes are unstable. The stereochemistry of the adducts **12** could not be determined.

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