1748 © 1990 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 63, 1748—1752 (1990) [Vol. 63, No. 6

New Near Infrared Absorbing Metal Complex Dyes: Synthesis and Metallochromic Properties of Two Isomeric Ligands, 2-(Dimethylamino)naphtho{[1,2-*g*] and [2, 1-*g*]}quinoline-7,12-diones

Katsuhira YOSHIDA,* Tetsunao KOUJIRI, Eriko SAKAMOTO, and Yuji KUBO
Department of Chemistry, Faculty of Science, Kochi University, Akebono-cho, Kochi 780

(Received February 10, 1990)

The Diels-Alder reaction of 5,8-quinolinedione with *p*-(dimethylamino)styrenes gave new two kinds of isomeric dyes, 2-(dimethylamino)naphtho[1,2-*g*]quinoline-7,12-diones and 2-(dimethylamino)naphtho[2,1-*g*]quinoline-7,12-diones, which showed quite different metallochromic behaviors. Upon addition of metal salts, one of the two isomers showed drastic spectral changes to have an intense absorption band in near infrared region. The color-structure relations were investigated.

Near infrared absorbing dyes have attracted considerable attention, since these organic dyes have prospect of many applications in the field of diode-laser optical storage or in other fields such as laser printer or color filter systems. However, organic dyes which can absorb at near infrared light are not numerous and are earnestly desired. Recently, we have proposed a new synthetic design of near infrared absorbing dyes by utilizing metallochromic properties of some quinonoid ligands,[1-4] the first absorption bands of which were drastically shifted to longer wavelengths with a large increase in the absorption intensity by metal chelate complexation.

In this paper, we report the synthesis of another type of quinonoid ligands obtained by the Diels-Alder type reaction of 5,8-quinolinedione(**1**) with *p*-(dimethylamino)styrenes (**2a**—**2c**). The reaction gave two kinds of isomeric dyes, **3a**—**3c** and **4a**—**4c** which can easily form metal chelate complexes with some metal ions. Very interestingly, in spite of quite resemblance of their absorption spectra in the free state, only one of the two isomers showed drastic spectral changes induced by metal chelate complexation and the resulting metal chelate complexes have intense absorption bands in near infrared region. The details are examined to assign the structure-color relations for the two isomers showing different metallochromic behaviors.

Results and Discussion

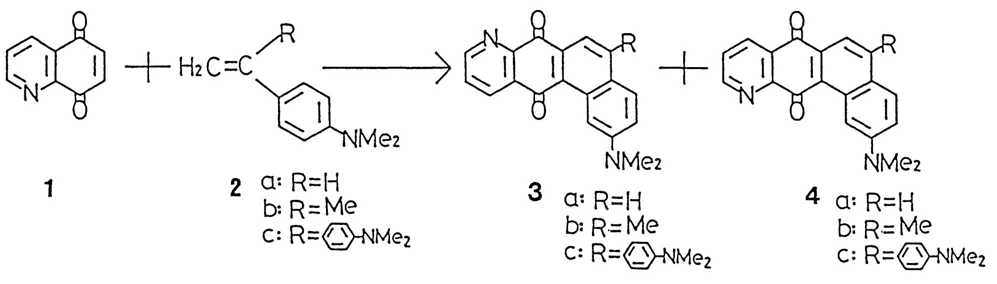
Syntheses of Isomeric Dyes (3a—3c and 4a—4c).

The thermal reaction of 1,4-naphthoquinone with some substituted styrenes is known to proceed via the Diels-Alder type reaction and to produce benz[*a*]anthracene-7,12-dione derivatives.[5-7] We examined the reaction of 5,8-quinolinedione (**1**), which is an aza analogue of 1,4-naphthoquinone, with *p*-(dimethylamino)styrenes (**2a**—**2c**) and found that 2-(dimethylamino)naphtho[1,2-*g*]quinoline-7,12-diones (**3a**—**3c**) and 2-(dimethylamino)naphtho[2,1-*g*]quinoline-7,12-diones (**4a**—**4c**) were obtained as shown in Scheme 1 and Table 1. The Diels-Alder type reaction of **1** with **2c** proceeded smoothly in a glass autoclave when various solvents except for pyridine were used. Especially when chloroform, benzene, or ethanol were used as solvents, the reaction proceeded efficiently to give

Table 1. The Reaction of 5,8-Quinolinedione (**1**) with *p*-(Dimethylamino)styrenes (**2a**—**2c**)[a]

Run	Styrene[b]	Solvent	Temp/°C	Time/h	Yield/%[a]	
	2				**3**	**4**
1	**2a**	$CHCl_3$	100	55	**3a** 13.5	**4a** 11.8
2	**2b**	$CHCl_3$	100	35	**3b** 26.1	**4b** 22.6
3	**2c**	$CHCl_3$	65	1	**3c** 33.5	**4c** 43.8
4	**2c**	CH_2Cl_2	40	2	**3c** 24.6	**4c** 18.8
5	**2c**	Benzene	80	3	**3c** 27.0	**4c** 34.8
6	**2c**	EtOH	80	2	**3c** 28.3	**4c** 39.3
7	**2c**	Pyridine	116	5	—[d]	—[d]

a) The reactions were conducted in a glass autoclave. b) Mole ratio; [1] : [2]=4 : 1. c) Isolated yield based on **2** used. d) Corresponding products were not obtained.



Scheme 1.

Table 2. The Analytical and Physical Data of the Two Isomers (**3a**—**3c** and **4a**—**4c**)

	3a	**3b**	**3c**
Mp (°C)	269—271	261—262	281—282
IR (KBr); cm^{-1}	1669, 1651 (C=O)	1667, 1652 (C=O)	1671, 1640 (C=O)
λ_{max} (ε_{max})	566 (4390)	563 (4250)	563 (6040)
in THF			485 (5580)
NMR; δ ppm	8.90—9.10 (2H, m, H^1 and H^9)	8.93 (1H, dd, *J*=1.8, 4.6 Hz, H^9)	8.95—9.05 (2H, m, H^1 and H^9)
	8.66 (1H, dd, *J*=1.6, 7.9 Hz, H^{11})	8.71 (1H, d, *J*=2.6 Hz, H^1)	8.62 (1H, dd, *J*=1.5, 8.0 Hz, H^{11})
	8.21 (1H, d, *J*=8.5 Hz, H^6)	8.47 (1H, dd, *J*=1.8, 7.9 Hz, H^{11})	8.10 (1H, s, H^6)
	8.06 (1H, d, *J*=8.5 Hz, H^5)	7.80 (1H, d, *J*=9.4 Hz, H^4)	7.97 (1H, d, *J*=9.6 Hz, H^4)
	7.79 (1H, d, *J*=9.2 Hz, H^4)	7.71 (1H, dd, *J*=4.6, 7.9 Hz, H^{10})	7.66 (1H, dd, *J*=4.6, 8.0 Hz, H^{10})
	7.71 (1H, dd, *J*=4.6, 7.9 Hz, H^{10})	7.71 (1H, s, H^6)	7.44 (2H, d, *J*=8.9 Hz)
	7.33 (1H, dd, *J*=2.6, 9.2 Hz, H^3)	7.11 (1H, dd, *J*=2.6, 9.4 Hz, H^3)	7.13 (1H, dd, *J*=2.6, 9.6 Hz, H^3)
	3.22 (6H, s, -NMe$_2$)	3.09 (6H, s, -NMe$_2$)	6.84 (2H, d, *J*=8.9 Hz)
	in CDCl$_3$	2.67 (3H, s, -CH$_3$)	3.16 (6H, s, -NMe$_2$)
		in CDCl$_3$: CD$_3$NO$_2$=1 : 1	3.05 (6H, s, -NMe$_2$)
			in CDCl$_3$
Anal.	C, 75.21 (75.48)	C, 75.61 (75.93)	C, 76.72 (76.94)
Found (Calcd)	H, 4.52 (4.67)	H, 4.93 (5.10)	H, 5.51 (5.50)
	N, 9.10 (9.27)	N, 8.82 (8.86)	N, 9.79 (9.97)
Mass (*m*/*z*)	302 (M$^+$)	316 (M$^+$)	421 (M$^+$)

	4a	**4b**	**4c**
Mp (°C)	244—246	266—268	264—265
IR (KBr); cm^{-1}	1667 (C=O)	1665 (C=O)	1663 (C=O)
λ_{max} (ε_{max})	566 (3950)	563 (3760)	562 (5600)
in THF			468 (5280)
NMR; δ ppm	9.0—9.1 (2H, m, H^1 and H^{10})	9.03 (1H, dd, *J*=1.4, 5.4 Hz, H^{10})	9.17 (1H, d, *J*=2.6 Hz, H^1)
	8.56 (1H, dd, *J*=1.8, 7.9 Hz, H^8)	8.95 (1H, d, *J*=2.4 Hz, H^1)	9.06 (1H, dd, *J*=1.8, 4.8 Hz, H^{10})
	8.06 (2H, s, H^5 and H^6)	8.48 (1H, dd, *J*=1.4, 8.1 Hz, H^8)	8.54 (1H, dd, *J*=1.8, 7.9 Hz, H^8)
	7.77 (1H, d, *J*=9.1 Hz, H^4)	7.97 (1H, d, *J*=9.2 Hz, H^4)	8.02 (1H, s, H^6)
	7.66 (1H, dd, *J*=4.6, 7.8 Hz, H^9)	7.80 (1H, s, H^6)	8.00 (1H, d, *J*=9.5 Hz, H^4)
	7.32 (1H, dd, *J*=2.3, 9.1 Hz, H^3)	7.72 (1H, dd, *J*=5.4, 8.1 Hz, H^9)	7.63 (1H, dd, *J*=4.8, 7.9 Hz, H^9)
	3.21 (6H, s, -NMe$_2$)	7.32 (1H, dd, *J*=2.4, 9.2 Hz, H^3)	7.44 (2H, d, *J*=9.0 Hz)
	in CDCl$_3$	3.18 (6H, s, -NMe$_2$)	7.19 (1H, dd, *J*=2.6, 9.5 Hz, H^3)
		2.75 (3H, s, -CH$_3$)	6.85 (2H, d, *J*=9.0 Hz)
		in CDCl$_3$: CD$_3$NO$_2$=1 : 1	3.20 (6H, s, -NMe$_2$)
			3.06 (6H, s, -NMe$_2$)
			in CDCl$_3$
Anal.	C, 75.33 (75.48)	C, 75.81 (75.93)	C, 77.11 (76.94)
Found (Calcd)	H, 4.38 (4.67)	H, 4.96 (5.10)	H, 5.47 (5.50)
	N, 9.21 (9.27)	N, 8.83 (8.86)	N,10.00 (9.97)
Mass (*m*/*z*)	302 (M$^+$)	316 (M$^+$)	421 (M$^+$)

Table 3. Spectral Data for the Complex Formation of Various Metal Salts with **4a**—**4c** in THF

Free ligand		Metal salt	Mole ratio$^{a)}$	Complex		$\Delta\lambda_{max}{}^{b)}$	$R\ \varepsilon_{max}{}^{c)}$
No.	$\lambda^F{}_{max}$ nm(ε_{max})		[Metal] / [Ligand]	Ratio Metal : Ligand	$\lambda^C{}_{max}$ nm(ε_{max})	nm	
4a	566(3950)	SnCl$_4$	1.6	1 : 1	824(11200)	258	2.84
4b	563(3760)	Cu(ClO$_4$)$_2$·6H$_2$O	0.5	1 : 2	807(17500)	244	4.65
		Ni (ClO$_4$)$_2$·6H$_2$O	0.4	1 : 3	730(21100)	167	5.61
		Co(ClO$_4$)$_2$·6H$_2$O	1.2	1 : 2	713(13800)	150	3.67
		SnCl$_4$	1.4	1 : 1	819(11300)	256	3.00
		SnCl$_4$·xH$_2$O	1.4	1 : 1	816(11400)	253	3.03
		InCl$_3$·4H$_2$O	6.0	1 : 1	745(6710)	182	1.78
4c	562(5600)	Cu(ClO$_4$)$_2$·6H$_2$O	0.5	1 : 2	794(26900)	232	4.80
		Ni (ClO$_4$)$_2$·6H$_2$O	0.4	1 : 3	690(38600)	128	6.89
		Co(ClO$_4$)$_2$·6H$_2$O	0.8	1 : 2	698(18900)	136	3.38
		SnCl$_4$	1.2	1 : 1	743(22800)	181	4.07

a) Mole ratio at which the spectral changes are saturated. b) $\Delta\lambda_{max}=\lambda^C{}_{max}$ (complex)$-\lambda^F{}_{max}$ (free ligand). c) $R\ \varepsilon_{max}=\varepsilon_{max}$ (complex)/ε_{max} (free ligand).

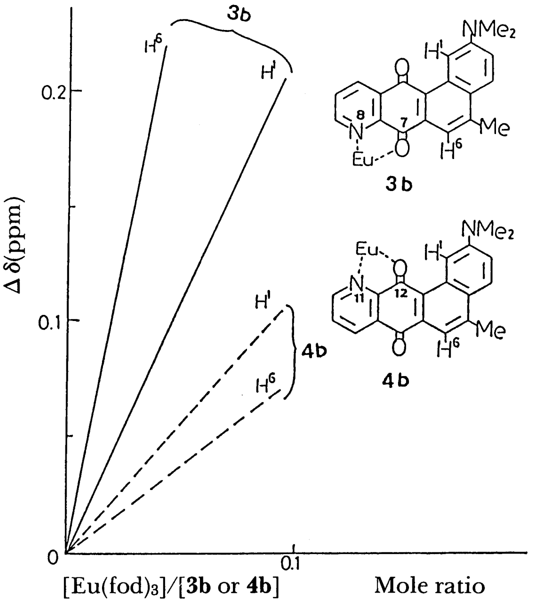


Fig. 1. Chemical shift changes by addition of Eu(fod)$_3$.

3c and **4c** in favorable yields (runs 3—6). Similarly, with other styrene derivatives (**2a** and **2b**) the reaction also gave the corresponding two isomeric compounds (**3a**, **3b**, and **4a**, **4b**) in lower yields. The reactivity of styrenes was the following order: **2a**<**2b**<**2c**. The assignment of the structures of two isomers (**3** and **4**) was performed by the method reported in the literature;[8] the location of nitrogen atom was confirmed by analyzing their ^{1}H NMR chemical shift changes of the ring protons induced by addition of Eu(fod)$_3$ as a chemical shift reagent. If the structure was **3**, the coordination of europium ion between the ring 8-nitrogen atom and 7-quinone carbonyl group would induce larger chemical shift of H^6 than that of H^1. On the contrary, if the structure was **4** the coordination of europium ion between 11-nitrogen atom and 12-quinone carbonyl group would induce larger chemical shift of H^1 than that of H^6. An example of the results for compounds (**3b** and **4b**) are shown in Fig. 1. On the basis of results, **3b** and **4b** were assigned to 2-dimethylamino-5-methylnaphtho[1,2-g]quinoline-7,12-dione and 2-dimethylamino-5-methylnaphtho[2,1-g]quinoline-7,12-dione, respectively. The physical and analytical data of the two kinds of isomers (**3a**—**3c** and **4a**—**4c**) are summarized in Table 2. In the IR spectra small difference was observed between the two isomers: the absorption bands of the two C=O groups were observed separately in the spectra of **3a**—**3c**, whereas overlapped each other in those of **4a**—**4c**. The UV-VIS spectra of the two isomers were very similar in their free states, however, quite different spectral changes were observed upon addition of metal salts.

Metallochromic Properties of Isomeric Dyes (3a—3c and 4a—4c). We have found that the isomeric dyes (**3** and **4**) can easily form metal chelate complexes between the ring nitrogen atom and neighboring quinone carbonyl group and that the absorption spectra of these dyes are changed by the metal complexation. Very interestingly, the features of spectral changes were quite different between the two isomers (**3** and **4**). As a typical example, Fig. 2 shows the spectral changes observed upon addition of tin(IV) chloride to THF solutions of **3b** and **4b**. In the case of **3b**, a new band appeared around 820 nm, however, only small increase in the absorption intensity of the new band was observed with further addition of the metal salt to the solution. On the other hand, in the case of **4b**, the absorption band around 563 nm due to the free ligand (**4b**) decreased with great increase in absorption intensity of a new band around 820 nm. The final absorption spectrum ([Sn^{4+}]/[**4b**]=1.2) had an intense absorption maximum at 819 nm in near infrared

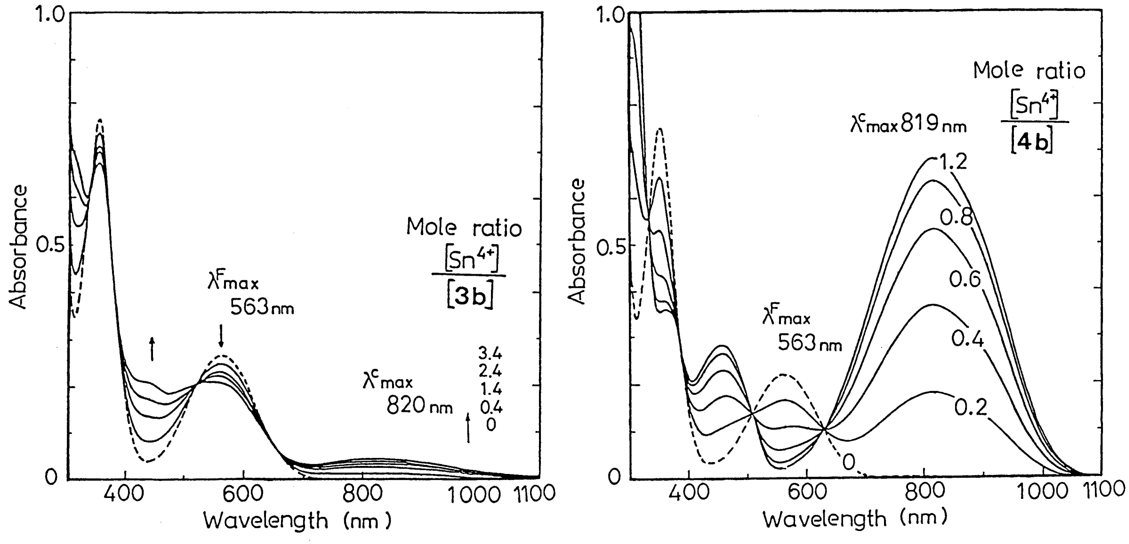


Fig. 2. Spectral changes uppon addition of SnCl$_4$ to the THF solution of **3b** and **4b**: [**3b**]=[**4b**]=6.25×10^{-5} M.

region. Isosbestic points were observed in both cases, which indicated the presence of a simple equilibrium in the solution. The similar spectral changes were also observed when other compounds (**3a**, **3c** and **4a**, **4c**) and other metal ions were used: every 3-isomers showed small spectral changes, whereas every 4-isomers showed drastical spectral changes. Consequently, it is concluded that the two isomers are easily distinguishable by comparing their spectral changes upon addition of the metal ions. We further investigated the details about the metal chelate complexations and drastic spectral changes of the isomers (**4a**—**4c**). The ratios of metal vs. ligand of the complexes formed in the solution were estimated by the continuous variation method. In Fig. 3, continuous variation plots are illustrated. The absorption maxima employed were those corresponding to new bands which appeared on addition of the metal ions. Figure 3 shows that maxima appear at [ligand]/([ligand]+[metal ion])=0.5, 0.67, and 0.75, suggesting the formation of 1 : 1, 1 : 2, and 1 : 3 metal-ligand complexes, respectively. Table 3 summarizes the spectral data for the complex formation of the isomers (**4a**—**4c**) with some metal ions in THF at 25 °C. The molecular extinction coefficient of the free ligand (**4c**) was larger than those of other free ligands (**4a** and **4b**), and similar tendency was also observed when they formed complexes with metal ions. The values of bathochromic shifts ($\Delta\lambda_{\max}=\lambda^{C}_{\max}$ (complex)-$\lambda^{F}_{\max}$ (free ligand)) induced by the complex formation of **4a** and **4b** were larger than that of **4c**. Both the bathochromic shift ($\Delta\lambda_{\max}$) and the relative ratio of absorption intensity ($R\varepsilon_{\max}=\varepsilon_{\max}$ (complex)/$\varepsilon_{\max}$ (free ligand)) were also dependent on the nature of metal ions participated in chelate complexation. The $\Delta\lambda_{\max}$ was in the range of 110—260 nm and the $R\varepsilon_{\max}$ was about 2—7 times. Especially, the Cu(II) or Sn(IV) complexes with the ligands (**4a**—**4c**) showed a large bathochromic shift (about 200—260 nm) and remarkable increase in the molecular extinction coefficient, and consequently they showed intense absorption bands in near infrared region. These metallochromic dyes are useful not only for practical applications but also for theoretical investigations of light absorption of metal complex dyes. The detailed mechanism for the drastic spectral changes induced by metal chelate complexation is now under investigation with the aid of MO calculations.

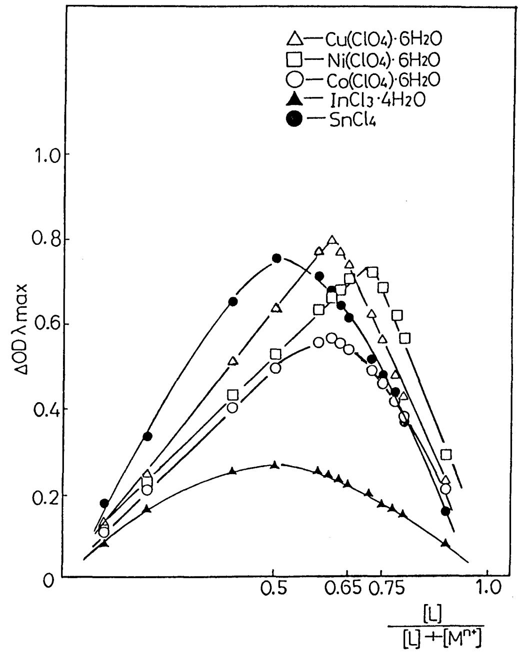


Fig. 3. Continuous variation plots for the Metal (M^{n+})-Ligand (**4b**) complexes in THF: $[M^{n+}]+[\mathbf{4b}]=1.25\times10^{-4}$ M.

Experimental

Measurements. All the melting points are uncorrected. UV and VIS spectra were measured with a Hitachi 220A spectrophotometer and a JASCO Ubest-30 spectrophotometer equipped with a temperature controller (JASCO EHC-363). ^{1}H NMR spectra were taken on a Hitachi Model R-90H spectrometer with TMS as the internal standard. IR spectra were obtained by using a JASCO FT/IR 5000 spectrometer on KBr pellets. Mass spectra were run on a Hitachi M-80A spectrometer and elemental analyses were recorded on a Perkin-Elmer 240 C CHN analyser. Thin layer chromatography was performed on silica gel (Merk kieselgel 60).

Materials. 5,8-Quinolinedione (**1**) was prepared according to a procedure described in the literature.[9] Metal perchlorate hexahydrates were prepared according to the methods described in the literature.[10,11] Metal chlorides were reagent-grade and were used without further purification. The solvents were purified by ordinary methods.

Preparation of *p*-(Dimethylamino)styrenes (2a—2c). A 300 ml three necked round-bottomed flask was fitted with a reflux condenser, an addition funnel, a magnetic stirrer, and a gas inlet tube. A gentle flow of argon through the apparatus was maintained throughout the reaction. A hexane solution of *n*-butyllithium (20 mmol, about 13 ml and 40 ml of anhydrous ether was added to the flask. The solution was stirred and triphenylmethylphosphonium bromide[12] (20 mmol) was added cautiously over a 15 min period. The solution was stirred for 4 h at room temperature. A solution containing the corresponding carbonyl compounds [*p*-(dimethylamino)benzaldehyde, *p*-(dimethylamino)acetophenone, or bis[*p*-dimethylamino)-phenyl]ketone in 100 ml of ether or benzene was added. The mixture was stirred at 25 °C (for **2a** and **2b**) or at 63 °C (for **2c**). The reaction was monitored by TLC analysis, and the existence of starting carbonyl compounds was checked by a carbonyl detecting reagent. After the starting carbonyl compounds was consumed (2—9 h), the precipitate was separated by suction filtration. The filtrate was concentrated in vacuo and the crude products were purified by column chromatography (silica gel: Wakogel C-300 using benzene as eluent).

p-(Dimethylamino)styrene (**2a**): Yield 42%, ^{1}H NMR ($CDCl_3$) δ=2.93 (6H, s), 5.00 (1H, dd, J=1.2 and 10.8 Hz), 5.52 (1H, dd, J=1.2 and 17.6 Hz), 6.63 (1H, dd, J=10.8 and

17.6 Hz), 6.67, 7.29 (4H, ABq, J=9.0 Hz).

2-[*p*-(Dimethylamino)phenyl]propene (**2b**): Yield 46%, ^{1}H NMR ($CDCl_3$) δ=2.12 (3H, m), 2.95 (6H, s), 4.95 (1H, m), 5.25 (1H, m), 6.68, 7.38 (4H, ABq, J=9.0 Hz).

1,1-Bis[*p*-(dimethylamino)phenyl]ethene (**2c**): Yield 94%, ^{1}H NMR ($CDCl_3$) δ=2.95 (12H, s), 5.18 (2H, s), 6.67, 7.26 (8H, ABq, J=9.0 Hz).

Reaction of 1 with 2a and 2b. The general procedure was as follows. A mixture of **1** (2.67 mmol) and **2** (0.667 mmol) in 10 ml of chloroform was reacted in a glass autoclave (TEM-MV Type: Taiatsu Glass Industry) with stirring and heating. The reaction was monitored by TLC analysis. After the starting material was consumed, the precipitate was separated by suction filtration. The filtrate was concentrated in vacuo and the residue containing the two main products (**3** and **4**) were chromatographed on activated alumina using chloroform and then on silica gel using ethyl acetate : benzene (=1 : 2) as eluent, and purified by recrystallization from chloroform.

Reaction of 1 with 2c. The reaction and treatment procedures were almost the same as those described above. The crude products were washed with small amount of ethanol and then chromatographed on silica gel using ethylacetate : dichloromethane (=1 : 1) as eluent and purified by recrystallization from chloroform.

The yields are summarized in Table 1. The analytical and physical data are summarized in Table 2.

The present work was partially supported by a Grant-in-Aid for Scientific Research (No. 01550676) from the Ministry of Education, Science and Culture. The authors thank the Research Center, Mitsubishi Kasei Corporation for mass spectral and elemental analyses.

References

1) K. Yoshida, M. Ishiguro, and Y. Kubo, *Chem. Lett.*, **1987**, 2057.

2) Y. Kubo, K. Sasaki, and K. Yoshida, *Chem. Lett.*, **1987**, 1663; Y. Kubo, K. Sasaki, H. Kataoka, and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1469.

3) Y. Kubo, H. Kataoka, and K. Yoshida, *J. Chem. Soc. Chem. Commun.*, **1988**, 1457; Y. Kubo, H. Kataoka, M. Ikezawa, and K. Yoshida, *J. Chem. Soc., Perkin Trans. 1*, **1990**, 585.

4) K. Yoshida, T. Koujiri, N. Oga, M. Ishiguro, and Y. Kubo, *J. Chem. Soc., Chem. Commun.*, **1989**, 708; *idem., J. Chem. Soc., Perkin Trans. 1*, in press.

5) K. Bansho, *Kogyo Kagaku Zasshi*, **63**, 1990 (1960).

6) J. E. Tomaszewski, W. B. Manning, and G. M. Muschik, *Tetrahedron Lett.*, **1977**, 921; W. B. Manning, J. E. Tomaszewski, G. M. Muschik, and R. I. Sato, *J. Org. Chem.*, **42**, 3465 (1977); W. B. Manning, G. M. Muschik, and J. E. Tomaszewski, *ibid.*, **44**, 699 (1979); G. M. Muschik, J. E. Tomaszewski, R. I. Sato, and W. B. Manning, *ibid.*, **44**, 2150 (1979).

7) M. Gates, *J. Org. Chem.*, **47**, 578 (1982).

8) K. Maruyama, S. Tai, and T. Otsuki, *Chem. Lett.*, **1981**, 1565; K. Maruyama, S. Tai, and T. Otsuki, *Heterocycles*, **20**, 1031 (1983).

9) Y. T. Pratt and N. L. Drake, *J. Am. Chem. Soc.*, **82**, 1155 (1960).

10) H. Ito, *Nippon Kagaku Zasshi*, **77**, 1383 (1956).

11) Nippon Kagakukai, "Shin Jikken Kagaku Koza," (1977), Vol. 8, p. 914 .

12) G. Wittig and U. Schoellkopf, *Org. Synth.*, Vol. 5, 751 (1973).