[Chem. Pharm. Bull.
34(1) 7—14 (1986)]

Studies on Tertiary Amine Oxides. LXXXII.[1] The Reaction of 1-Oxido-4(or 2)-pyridinediazonium Tetrafluoroborate with Olefins in the Presence of Palladium Complex

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(Received April 30, 1985)

1-Oxido-4-pyridinediazonium tetrafluoroborate (4-PFB) reacts with olefins (cyclopentene, styrene, ethyl acrylate, indene, cyclohexene, cyclooctene, 1-octene and 1-dodecene) in the presence of tris(dibenzylideneacetone)dipalladium to afford the corresponding alkenylated products (**1**, **2**, **3**, **4**, **5**, **6**, **7** and **8**) in good yields.

1,2,3,5-Oxatriazolo[5,4-*a*]pyridinium tetrafluoroborate (2-PFB) also reacts with cyclopentene and styrene to give 2-cyclopentenylpyridine 1-oxides (**13** and **14**) and (*E*)-2-(α-styryl)pyridine 1-oxide (**15**), respectively, in low yields.

Keywords——aromatic N-oxide; alkenylpyridine N-oxide; alkenylation; palladium complex; aminopyridine diazonium tetrafluoroborate

In previous studies on displacement reactions with carbon substituents at the 4-position of pyridine and quinoline 1-oxides, we showed that 4- and 2-aminopyridine 1-oxides underwent pseudo-Gomberg reaction to afford the arylated products in fairly good yields.[2] In this work, the reaction of 4-pyridinediazonium tetrafluoroborate with olefins in the presence of palladium complex was examined as an extension of our studies on carbon substitution reactions of the pyridine ring. The carbon substitution reaction using an aromatic diazonium salt is well-known as the so-called "Meerwein reaction."[3] Elliott *et al.*[4] have reported that the reactions of a mixture of aromatic amines and olefins with alkyl nitrite afforded alkenylation products in good yields.

The reactions of 4-aminopyridine 1-oxide with 2,3-dihydropyrane and cyclopentene were attempted according to Elliott's procedure, but failed. Recently, it was reported by Matsuda *et al.*[5] that the reactions of aromatic diazonium salts with alkenes in the presence of palladium complex proceeded smoothly to give the alkenylated aromatics in good yields.

The reaction of 1-oxido-4-pyridinediazonium tetrafluoroborate (4-PFB)[6] with cyclopentene catalyzed by tris(dibenzylideneacetone)dipalladium [$(dba)_3Pd_2$] was found to proceed successfully to afford 4-(1-cyclopentenyl)pyridine 1-oxide (**1**) in a yield of 76%. The mass spectrum (MS) of **1** gave the molecular ion peak at *m/z*: 161. The proton magnetic resonance (^{1}H-NMR) spectrum ($CDCl_3$) showed a two-proton doublet at δ: 8.11 (J=7.0 Hz) assigned to C_2- and C_6-protons of the pyridine ring, a two-proton doublet at δ: 7.26 (J=7.0 Hz), assigned to C_3- and C_5-protons of the pyridine ring, a one-proton multiplet at δ: 6.36 due to the vinylic proton and other peaks due to the cyclopentene ring protons. The presence of the signal due to one vinylic proton revealed that the double bond was conjugated with the pyridine ring. These spectral data are consistent with the structure **1**. Subsequently, the reactions of 4-PFB with styrene, ethyl acrylate, indene, cyclohexene, cyclooctene, 1-octene and 1-dodecene were investigated. The reaction products and their yields are shown in Chart 1.

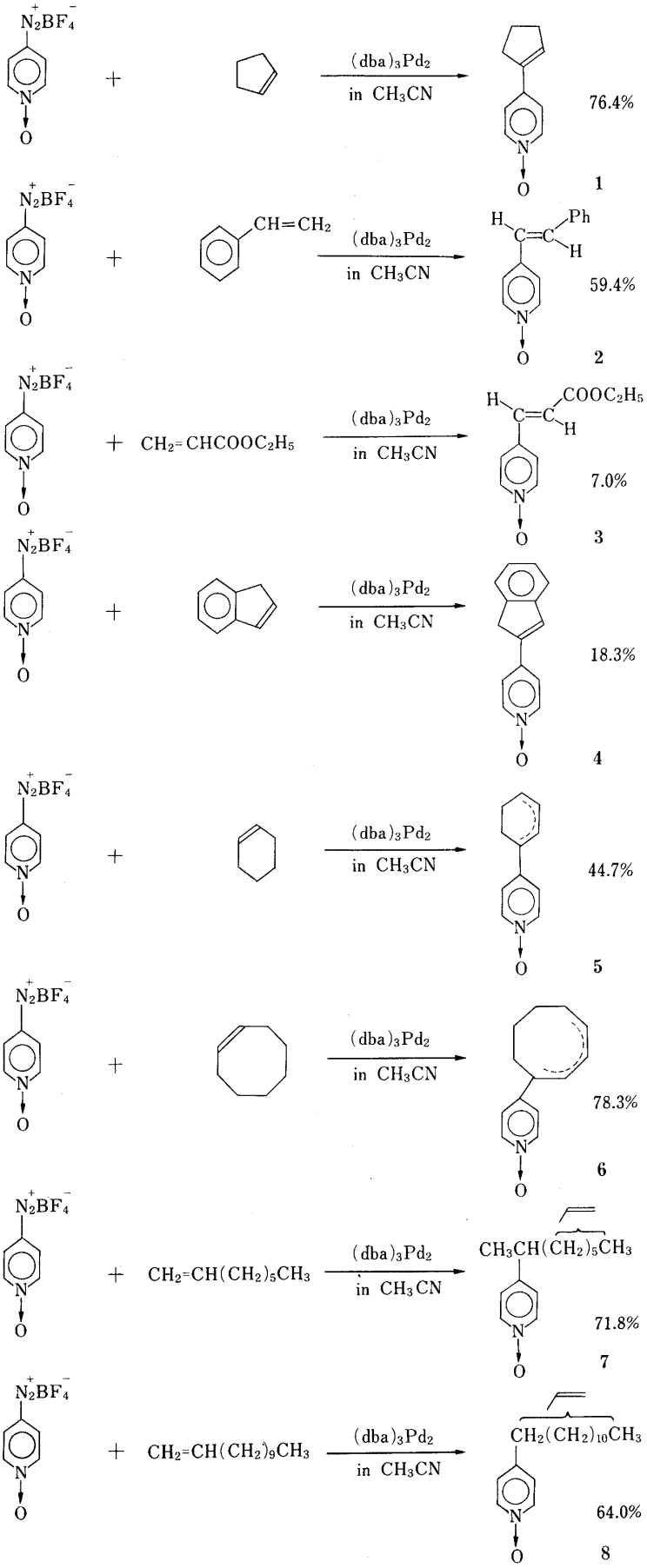

Chart 1

Styrene was allowed to react with 4-PFB to give (*E*)-4-(α-styryl)pyridine 1-oxide (**2**) in 59% yield. The reaction of 4-PFB with ethyl acrylate gave 4-[1-((*E*)-2-ethoxycarbonyl-vinyl)]pyridine 1-oxide (**3**) in a low yield of 7%. MS of **2** and **3** showed the molecular ion peaks at *m/z*: 197 and 193, respectively. The infrared (IR) spectrum of **2** exhibited absorptions at 1630 and 967 cm^{-1} and that of **3** showed absorptions at 1640 and 982 cm^{-1}, indicating that **2** and **3** are *trans*-disubstituted ethylenes.[7] Furthermore, in view of the fact that the ^{1}H-NMR spectra of **2** and **3** exhibited peaks due to olefinic protons with *trans* coupling constants (J=16.5 and 16.0 Hz, respectively), it was clear that the double bond could be assigned the *E*-configuration. Indene was allowed to react to give 4-(2-indenyl)pyridine 1-oxide (**4**) in a yield of 18.3%. The MS of **4** showed the molecular ion peak at *m/z*: 209. The ^{1}H-NMR spectrum ($CDCl_3$) exhibited a two-proton singlet at δ: 3.71 due to the C_3-protons of the indene, indicating that substitution had taken place at the 2-position of indene.

Reactions of cyclohexene, cyclooctene, 1-octene, and 1-dodecene with 4-PFB proceeded smoothly to give pale yellow oils (**5**, **6**, **7**, and **8**, respectively) after chromatographic separation on silica gel. These oily products were assumed to be mixtures of positional isomers of the double bond. In order to determine whether the double bond of the product is conjugated with the pyridine ring or not, the ultraviolet (UV) spectra were measured, and isomerization of the double bond was found to have occurred in some cases.

Pyridine 1-oxide shows an absorption maximum at 264 nm, whereas the product **1** shows a longer-wavelength maximum at 303 nm. This bathochromic shift is apparently due to conjugation of the double bond with the pyridine ring. The products **6** and **7** absorbed at 300 and 292 nm, respectively, again indicating conjugation with the pyridine ring. On the other hand, **5** and **8** show absorption maxima at 269 and 268 nm, respectively. These absorptions are similar to that of pyridine 1-oxide, indicating the absence of conjugation of the double bond with the pyridine ring.

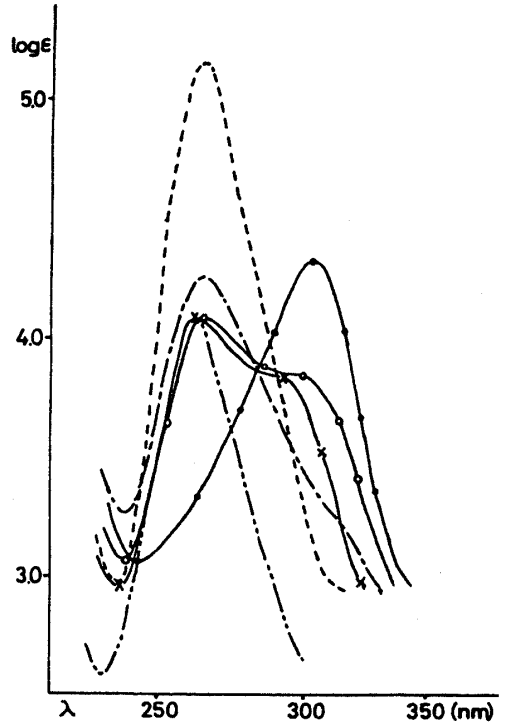

Fig. 1. Ultraviolet Spectra (in 95% EtOH) of Pyridine 1-Oxide, **1**, **5**, **6**, **7**, and **8**

----, O←N⟨⟩; ●—●, **1**; ------, **5**; ○—○, **6**; ×—×, **7**; — · —, **8**.

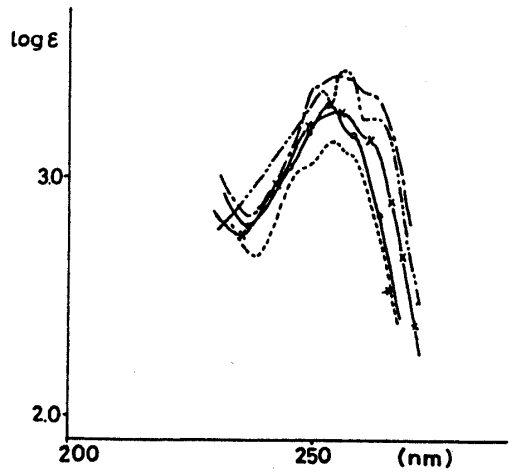

Fig. 2. Ultraviolet Spectra (in 95% EtOH) of Pyridine, **9**, **10**, **11**, and **12**

----, N⟨⟩; ------, **9**; ○—○, **10**; ×—×, **11**; — · —, **12**.

The purification of **5**, **6** and **7** could not be achieved, because these products were mixtures of positional isomers of the double bond which exhibited almost the same behavior on chromatography. Hence, these compounds were reduced to the pure dihydrogenated products and the structures were established by elemental analyses, and IR, ^{1}H-NMR, and MS studies. The hydrogenated products (**9**, **10**, and **11**) were obtained as colorless oils. The UV spectra of **9**, **10** and **11** were very similar to that of pyridine, as shown in Fig. 2, and the MS gave the molecular ion peaks at *m/z*: 161, 189, and 191, respectively.

The elemental analyses and IR spectral data were also consistent with the assigned structures (**9**, **10**, and **11**). Therefore, compounds **9** and **10** were identified as 4-cyclohexylpyridine and 4-cyclooctylpyridine, respectively. Compound **11** was established to be 4-(2-octyl)pyridine on the basis of the fact that the ^{1}H-NMR spectrum ($CDCl_3$) exhibited a one-proton multiplet at δ: 2.76—2.26 due to CH bearing a pyridyl group.

Because of the poor reactivity of **8** in hydrogenation, deoxygenation of **8** with phosphorus trichloride was carried out to give **12**. The UV spectrum of **12** was similar to that of pyridine, and the MS showed the molecular ion peak at *m/z*: 245. In view of the fact that ^{1}H-NMR ($CDCl_3$) of **12** showed a two-proton multiplet at δ: 2.60—2.19, in contrast to the case of **11**, the structure of **12** was assigned as 4-dodecenylpyridines, in which dodecene carries the pyridine group at the terminal carbon. It is not clear why the reaction proceeds *via* different routs in the case of 1-octene and 1-dodecene.

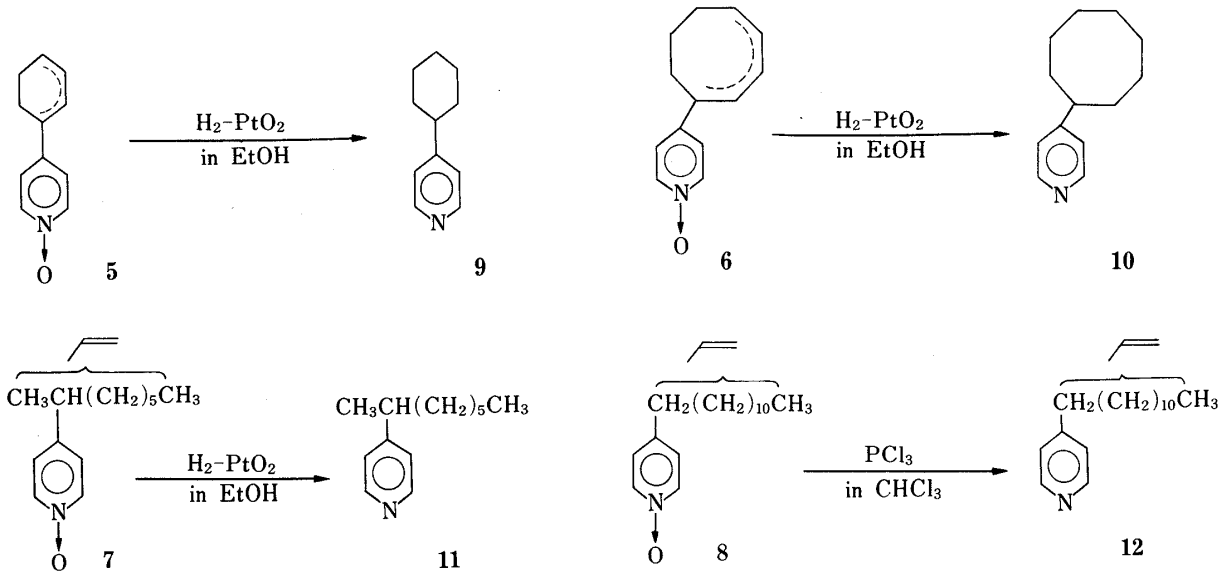

Chart 2

Next, alkenylation of 2-aminopyridine 1-oxide was examined. An acetonitrile solution of 1,2,3,5-oxatriazolo[5,4-*a*]pyridinium tetrafluoroborate (2-PFB)[6] was added to a mixture of $(dba)_3Pd_2$ and cyclopentene in acetonitrile under ice cooling. After the reaction was completed, chromatographic separation on silica gel gave the product as a viscous pale yellow oil in a yield of 29%. This oily substance was further purified by preparative thin layer chromatography. The fraction with $Rf=0.61$ was led to the picrate, mp 133.5—134.5 °C. The free base (**13**) was obtained from this picrate as colorless needles, mp 65—67 °C. The MS of **13** showed the molecular ion peak at *m/z*: 161. The ^{1}H-NMR spectrum ($CDCl_3$) exhibited a one-proton multiplet at δ: 6.96—7.11 due to the C_2-proton of cyclopentene. Compound **13** was assigned as 2-(1-cyclopentenyl)pyridine 1-oxide based on these spectral data. The fraction with $Rf=0.45$ was also led to the picrate, mp 125—126 °C. The free base (**14**) was obtained from this picrate as a pale yellow oil. Its MS showed the molecular ion peak at *m/z*: 161 and the ^{1}H-NMR

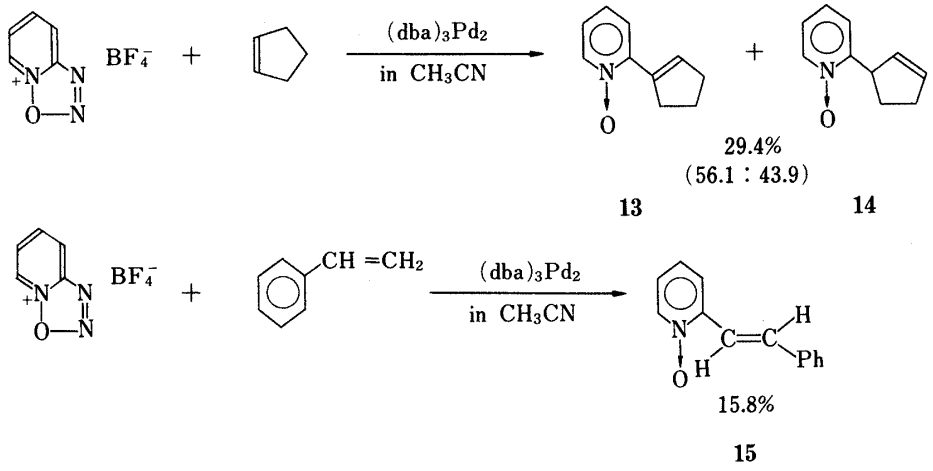

Chart 3

TABLE I. Spectral Data for the Products

Compounds	MS (M^+)	IR (cm^{-1}, Nujol)	NMR (δ, $CDCl_3$)
1	161	1620 (C=C) 1250 (N–O)	8.11 (2H, d, J=7.0 Hz, Py-H_2, H_6), 7.26 (2H, d, J=7.0 Hz, Py-H_3, H_5), 6.36 (1H, m, cyclopentene-H_2), 2.50—2.84 (4H, m, cyclopentene-H_3, H_5), 1.92—2.20 (2H, m, cyclopentene-H_4)
2	197	1630 (C=C) 1260 (N–O) 967 (C–H)	8.13 (2H, d, J=7.0 Hz, Py-H_2, H_6), 7.34 (2H, d, J=7.0 Hz, Py-H_3, H_5), 7.23—7.57 (5H, m, Ph-H), 7.16 (1H, d, J=16.5 Hz), 6.92 (1H, d, J=16.5 Hz)
3	193	1640 (C=C) 1270 (C–O–C) 1258 (N–O) 1170 (C–O–C) 982 (C–H)	8.17 (2H, d, J=7.0 Hz, Py-H_2, H_6), 7.53 (1H, d, J=16 Hz, ethyl acrylate-H_3), 7.38 (2H, d, J=7.0 Hz, Py-H_3, H_5), 6.46 (1H, d, J=16 Hz, ethyl acrylate-H_2), 4.27 (2H, q, J=7.9 Hz, $-CH_2-$), 1.34 (3H, t, J=7.9 Hz, CH_3)
4	209	1260 (N–O)	8.15 (2H, d, J=7.0 Hz, Py-H_2, H_6), 7.42 (2H, d, J=7.0 Hz, Py-H_3, H_5), 7.20—7.37 (7H, m, indene-H_3), 3.71 (2H, s, indene-H_3)
9	161	1598 (C=C or C=N) 1557 (C=C or C=N)	8.47 (2H, dd, $J_{2,3}$=6.0 Hz, $J_{2,5}$=0.9 Hz, Py-H_2, H_6), 7.11 (2H, dd, $J_{2,3}$=6.0 Hz, $J_{3,5}$=1.5 Hz, Py-H_3, H_5), 2.50 (1H, m, cyclohexane-H_1), 1.32—1.92 (10H, m, cyclohexane-H)
10	189	1598 (C=C or C=N) 1557 (C=C or C=N)	8.44 (2H, dd, $J_{2,3}$=6.0 Hz, $J_{2,5}$=0.9 Hz, Py-H_2, H_6), 7.09 (2H, dd, $J_{2,3}$=6.0 Hz, $J_{3,5}$=1.5 Hz, Py-H_3, H_5), 2.90—2.60 (1H, m, cyclooctane-H_1), 1.64—1.82 (14H, m, cyclooctane-H)
11	191	1600 (C=C or C=N) 1558 (C=C or C=N)	8.46 (2H, dd, $J_{2,3}$=6.0 Hz, $J_{2,5}$=0.9 Hz, Py-H_2, H_6), 7.02—7.12 (2H, m, Py-H_3, H_5), 2.76—2.26 (1H, m, octane-H_2), 1.72—0.68 (16H, m, octane-H)
12	245	1598 (C=C or C=N) 967 (C–H)	8.46 (2H, dd, $J_{2,3}$=6.0 Hz, $J_{2,5}$=0.9 Hz, Py-H_2, H_6), 7.10—7.00 (2H, m, Py-H_3, H_5), 5.50—5.17 (1.8H, m, vinyl-H), 2.60—2.19 (1.8H, m, dodecene-H_1), 2.00—0.70 (19H, m, dodecene-H)
13	161	1600 (C=C) 1250 (N–O)	8.24 (1H, dd, $J_{5,6}$=7.0 Hz, $J_{4,6}$=2.0 Hz, Py-H_6), 7.68—7.77 (1H, m, Py-H_4), 7.14—7.34 (2H, m, Py-H_3, H_5), 6.96—7.11 (1H, m, cyclopentene-H_2), 2.55—2.86 (4H, m, cyclopentene-H_3, H_5), 1.84—2.14 (2H, m, cyclopentene-H_4)
14	161	1610 (C=C) 1230 (N–O)	8.25 (1H, dd, $J_{5,6}$=7.0 Hz, $J_{4,6}$=2.0 Hz, Py-H_6), 7.02—7.34 (3H, m, Py-H_3, H_4, H_5), 6.02—6.15 (1H, m, cyclopentene-H_2), 5.70—5.82 (1H, m, cyclopentene-H_1), 4.48—4.78 (1H, m, cyclopentene-H_3), 1.60—2.80 (4H, m, cyclopentene-H_4, H_5)
15	197	1630 (C=C) 1240 (N–O) 968 (C–H)	8.21 (1H, dd, $J_{5,6}$=6.1 Hz, $J_{4,6}$=1.8 Hz, Py-H_6), 7.90—7.00 (10H, m, Py-H_3, H_4, H_5, styrene-H)

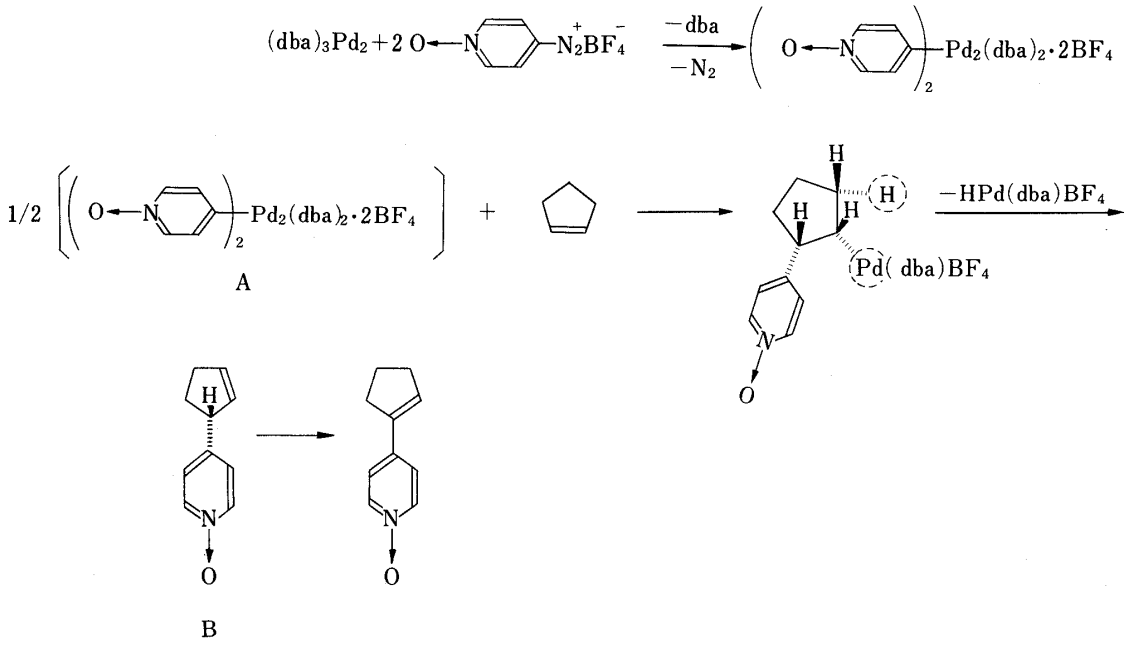

Chart 4

TABLE II. Elemental Analysis Data for the Products

Compounds	Formula	Analysis (%) Calcd (Found)		
		C	H	N
1	$C_{10}H_{11}NO$	74.51	6.88	8.69
		(74.18	6.88	8.59)
2	$C_{13}H_{11}NO$	79.16	5.62	7.10
		(79.02	5.73	7.01)
3	$C_{10}H_{11}NO_3$	62.16	5.74	7.25
		(61.98	5.82	7.18)
4	$C_{14}H_{11}NO$	80.36	5.30	6.69
		(79.91	5.37	6.61)
9	$C_{11}H_{15}N$	81.93	9.38	8.69
		(81.66	9.45	8.70)
10	$C_{13}H_{19}N$	82.48	10.12	7.40
		(82.03	10.20	7.37)
11	$C_{13}H_{21}N$	81.61	11.06	7.32
		(80.82	11.17	7.18)
12	$C_{17}H_{27}N$	83.20	11.09	5.70
		(83.00	11.14	5.65)
13-picrate	$C_{16}H_{14}N_4O_8$	49.23	3.62	14.36
		(49.27	3.72	14.15)
13-HCl	$C_{10}H_{12}ClNO$	60.76	6.12	7.09
		(60.84	6.17	6.81)
14-picrate	$C_{16}H_{14}N_4O_8$	49.23	3.62	14.36
		(49.13	3.68	14.14)
14-HCl	$C_{10}H_{12}ClNO$	60.76	6.12	7.09
		(60.66	6.15	6.91)
15	$C_{13}H_{11}NO$	79.16	5.62	7.10
		(79.20	5.67	7.03)

spectrum ($CDCl_3$) exhibited signals at δ: 6.02—6.15 (1H, m) due to the C_2-proton on cyclopentene and at δ: 4.48—4.78 (1H, m) due to the C_3-proton on cyclopentene. These spectral data are consistent with the structure **14**, 2-(2-cyclopentenyl)pyridine 1-oxide. The ratio of product **13** and **14** was *ca.* 56.1 : 43.9. The reaction of 2-PFB with styrene proceeded to give (*E*)-2-(α-styryl)pyridine 1-oxide (**15**) in 15.8% yield. The MS of **15** showed the molecular ion peak at *m/z*: 197 and its IR spectrum exhibited absorptions at 1630 and 968 cm^{-1} due to a *trans*-disubstituted double bond.[7] These spectral data are consistent with the structure **15**.

For the reaction of bromobenzene with *cis*- and *trans*-methylstyrene in the presence of palladium acetate, Heck[8] suggested the following mechanism, involving the initial *cis*-addition of the palladium complex, and subsequent *cis*-elimination of the palladium hydride. The mechanism of the present reaction may also involve *cis*-addition of the complex A generated *via* reaction of 4-PFB with $(dba)_3Pd_2$ to cyclopentene, followed by *cis*-elimination of the palladium hydride to form B and isomerization of the double bond to give **1**, as shown in Chart 4.

In conclution, the diazonium salt (4-PFB or 2-PFB) prepared from 4- or 2-aminopyridine 1-oxide was found to undergo novel alkenylation reactions.

Experimental

All melting points are uncorrected. IR spectra were recorded on a JASCO IR-E spectrometer. NMR spectra were measured with a JEOL PS-100 spectrometer at 100 MHz using tetramethylsilane (TMS) as an internal reference. MS were obtained on a JMS 01SG spectrometer. Preparative thin-layer chromatography (TLC) was performed on Kieselgel 60 PF_{245} (Merck, 20 × 20 cm).

General Procedure for Reaction of 4-PFB with Alkenes——A solution of 1 mmol of 4-PFB in 10 ml of CH_3CN was added to a mixture of 2 mmol of an alkene and 30 mg of $(dba)_3Pd_2$ in 10 ml of CH_3CN. The whole was stirred for 1 h, then the solvent was distilled off under reduced pressure. The residue was extracted with 10% HCl solution, made alkaline with 10% K_2CO_3 solution and extracted with CH_2Cl_2. The extract was dried on $MgSO_4$, CH_2Cl_2 was distilled off and the residue was purified by chromatography.

4-(1-Cyclopentenyl)pyridine 1-Oxide (1)——Cyclopentene (136 mg) was reacted as above with 200 mg of 4-PFB in the presence of 30 mg of $(dba)_3Pd_2$. Chromatography on silica gel gave 108.2 mg (76.4%) of **1** from the fraction eluted with CH_2Cl_2–MeOH (95 : 5), as colorless needles, mp 178—179 °C (hexane–CH_2Cl_2).

4-(α-Styryl)pyridine 1-Oxide (2)——Styrene (209 mg) was reacted as above with 200 mg of 4-PFB in the presence of 30 mg of $(dba)_3Pd_2$. Chromatographic separation on silica gel gave 112 mg of **2** from the fraction eluted with CH_2Cl_2–MeOH (95 : 5), as colorless needles, mp 167—169 °C (benzene).

4-[1-((*E*)-2-Ethoxycarbonylvinyl)]pyridine 1-Oxide (3)——Ethyl acrylate (200 mg) was reacted as above with 200 mg of 4-PFB in the presence of 30 mg of $(dba)_3Pd_2$ and the product was subjected to preparative TLC. The fraction with Rf=0.45 (CH_2Cl_2 : Me_2CO : MeOH = 7 : 2 : 1) gave **3** in 7.0% yield, as pale yellow needles, mp 141.5—142 °C (benzene).

4-(2-Indenyl)pyridine 1-Oxide (4)——Indene (232 mg) was reacted as above with 200 mg of 4-PFB in the presence of 30 mg of $(dba)_3Pd_2$ and the product was subjected to preparative TLC. The fraction with Rf=0.38 (CH_2Cl_2 : Me_2CO : MeOH = 7 : 2 : 1) gave 37 mg of **4**, as pale yellow needles, mp 181.5—182.5 °C (benzene).

4-Cyclohexenylpyridine (9)——Cyclohexene (165 mg) was reacted with 200 mg of 4-PFB in the presence of 30 mg of $(dba)_3Pd_2$. Chromatography on silica gel, eluting with CH_2Cl_2–MeOH (95 : 5), gave 75 mg (44.7%) of **5** as a pale yellow viscous oil. A solution of 100 mg of **5** in 12 ml of EtOH was subjected to hydrogenation in the presence of PtO_2 (5 mg). After the absorption of hydrogen (30 ml) had ceased, the solvent was distilled off and the residue was chromatographed on silica gel. The eluate with CH_2Cl_2 gave 77 mg (83.7%) of **9** as a colorless oil, bp 120 °C (1.6—1.3 mmHg, bath temperature).

4-Cyclooctylpyridine (10)——Cyclooctene (220 mg) was reacted with 200 mg of 4-PFB in the presence of 30 mg of $(dba)_3Pd_2$. Chromatography on silica gel gave 152 mg (78.2%) of **6** from the eluate with CH_2Cl_2–MeOH (95 : 5), as a pale yellow viscous oil. A solution of 120 mg of **6** in 15 ml of EtOH was subjected to hydrogenation in the presence of 5 mg of PtO_2 at room temperature. After the absorption of hydrogen (18 ml) had ceased, the solvent was distilled off and the residue was chromatographed on silica gel. The eluate with CH_2Cl_2 gave **10** as a colorless oil, bp 180 °C (1—1.2 mmHg, bath temperature).

4-(2-Octyl)pyridine (11)——1-Octene (224 mg) was reacted with 200 mg of 4-PFB in the presence of 30 mg of $(dba)_3Pd_2$. Chromatographic separation on silica gel gave 141 mg (71.8%) of **7** from the fraction eluted with CH_2Cl_2–MeOH (95 : 5), as a pale yellow viscous oil. A solution of 202 mg of **7** in 10 ml of EtOH was subjected to

hydrogenation in the presence of 5 mg of PtO_2. After the absorption of hydrogen (37 ml) had ceased, the solvent was distilled off and the residue was chromatographed on silica gel. The eluate with CH_2Cl_2 gave **11** as a colorless oil, bp 110 °C (0.4—0.6 mmHg, bath temperature).

4-Dodecenylpyridine (12)——1-Dodecene (338 mg) was reacted with 200 mg of 4-PFB in the presence of 30 mg of $(dba)_3Pd_2$. Chromatographic separation on silica gel gave 160 mg of **8** as a pale yellow oil from the fraction eluted with CH_2Cl_2–MeOH (95 : 5). PCl_3 (3 g) was added to a solution of 1.06 g of **8** in 10 ml of $CHCl_3$ under ice cooling. After being refluxed for 20 min, the reaction mixture was poured into ice water. The solution was made alkaline with K_2CO_3 and extracted with $CHCl_3$. The extract was dried over $MgSO_4$, the solvent was distilled off and the residue was chromatographed on alumina to give **12** from the fraction eluted with benzene, as a colorless oil, bp 145—165 °C (0.25 mmHg, bath temperature).

2-(1-Cyclopentenyl)pyridine 1-Oxide (13) and 2-(3-Cyclopentenyl)pyridine 1-Oxide (14)——A solution of 2 g of 2-PFB in 25 ml of the same solvent was added to a mixture of 1.36 g (20 mmol) of cyclopentene and 300 mg of $(dba)_3Pd_2$ in CH_3CN. Stirring was continued for 30 min at 40 °C. After treatment as described above, the crude product was purified by chromatography on silica gel. The eluate with CH_2Cl_2–MeOH (98 : 2) was further purified by preparative TLC. The fraction with $Rf=0.61$ (the first developing solvent was $CH_2Cl_2 : Me_2CO : MeOH = 8 : 2 : 1$, and the second developing solvent was $CH_2Cl_2 : MeOH = 9 : 1$) gave 254 mg (16.5%) of **13**, and the fraction with $Rf=0.45$ gave 199 mg (12.9%) of **14**. Picrates of **13** and **14** were obtained as pale yellow needles, mp 133.5—134.5 °C (EtOH) and mp 125—126 °C (EtOH), respectively. The hydrochlorides of **13** and **14** were obtained as colorless needles and colorless prisms, mp 143—145 °C (Me_2CO) and mp 115—116 °C (benzene), respectively.

(*E*)-2-(α-Styryl)pyridine 1-Oxide (15)——A solution of 2.1 g of 2-PFB in 25 ml of CH_3CN was added to a mixture of 2.1 g of styrene and 300 mg of $(dba)_3Pd_2$ in 25 ml of CH_3CN. Stirring was continued for 30 min at 40 °C. The solvent was distilled off, and the residue was made alkaline with 10% K_2CO_3 solution then extracted with CH_2Cl_2. Chromatography of the extract on silica gel gave 330 mg (15.8%) of **15** from the fraction eluted with CH_2Cl_2–MeOH (98 : 2), as colorless needles, mp 166—167 °C (benzene–hexane).

References

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