Direct C≡C Triple Bond Formation from the C=C Double Bond and Direct Hydroxylation into the *o*-Position of a Nitro Group on the Benzene Nucleus with Potassium *t*-Butoxide in *N*,*N*-Dimethylformamide in the Air#

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A novel and facile method for direct C≡C acetylenic bond formation from the C=C double bond by treatment with potassium *t*-butoxide (*t*-BuOK) in *N*,*N*-dimethylformamide in the air has been found in a 9, 10-bis(4-substituted styryl)anthracene series, in 4-substituted 4′-nitrostilbene series, and in 1-(*p*-nitrophenyl)-4-(*p*-substituted phenyl)-1,3-butadiene series; its scope and limitations have been examined. The ESR spectrum of the reaction against 4-diethylamino-4′-nitrostilbene was measured to identify an anion radical species expected for explanation of the mechanism of the dehydrogenation reaction. Further, cyclic voltammetric measurements of a series of stilbenes and diphenylacetylenes were carried out in connection with the above mechanism. In many cases, interestingly, the use of a large excess of *t*-BuOK brought about succeeding hydroxylation into the ortho-position of a nitro group on the benzene nucleus. The simple hydroxylation is useful for the synthesis of substituted 5-(arylethynyl)-2-nitrophenols, which are expected to function as non-linear optical materials with the corresponding non-hydroxy compounds. The ultraviolet-visible and fluorescence spectral properties were measured and discussed also with those of the related compounds.

The formation of a carbon–carbon triple bond from a carbon–carbon double bond is a fundamental process in synthetic organic chemistry. The development of methods of formation of the C≡C triple bond in organic structures has been fully reviewed in recent years.[1] The orthodox method of formation of the acetylenic bond is elimination of a stable substance from a more saturated structure. In the above references, the major elimination route has involved the removal of hydrogen halide molecules, i.e. dehydrohalogenation. About ten years ago, the direct conversion of terminal and internal monoalkenes into the corresponding alkynes was reported by Cum et al. who employed a heterogenized palladium(II) acetate catalyst in the presence of oxygen and perchloric acid in ethanol–water.[2]

In this paper, we report a novel and facile method for direct acetylenic bond formation by dehydrogenation from the C=C double bond by treatment with potassium *t*-butoxide (*t*-BuOK) in *N*,*N*-dimethylformamide (DMF) in the air. We have applied this method to three series of compounds: (i) 9,10-bis(4-substituted styryl)anthracenes (**1**); (ii) 4-substituted 4′-nitrostilbenes (**3**) and 1-(*p*-nitrophenyl)-4-(*p*-substituted phenyl)-1, 3-butadienes (**3′**); and (iii) *p*-nitrostyryl derivatives (**7**) (Table 1); its scope and limitations have been examined. The series of compounds (**2**) are particularly interesting in the field of peroxyoxalate chemiluminescence (CL) as enhancers.[3] The series of compounds (ii) and (iii) are remarkable for the possible use as donor–acceptor acetylene compounds for nonlinear optical materials.[4] In many cases of (ii) and (iii), interestingly, the use of a large excess of *t*-BuOK brought about hydroxylation into the ortho-position of a nitro group on the benzene nucleus (**5**, **5′**, **6**, **6′**, **9**, and **10**) (Table 1). The simple hydroxylation is useful for the synthesis of substituted 2-nitrophenols. The ultraviolet-visible (UV) and fluorescence (FL) spectra of compounds **3**—**10** were measured and results are discussed. By measuring the ESR spectrum through the process of the direct conversion of 4-diethylamino-4′-nitrostilbene (**3b**) to the corresponding acetylene (**4b**), the existence of an anion radical

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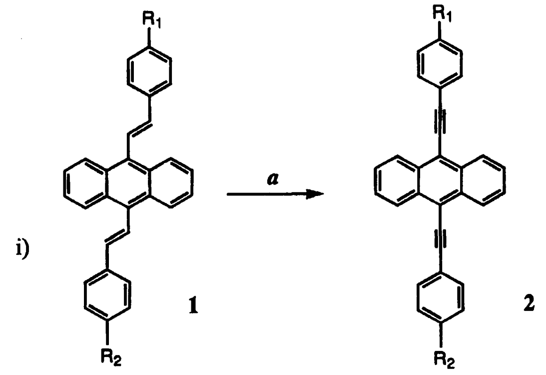
#The paper is dedicated to Prof. Emeritus Masazumi Nakagawa of Osaka University.

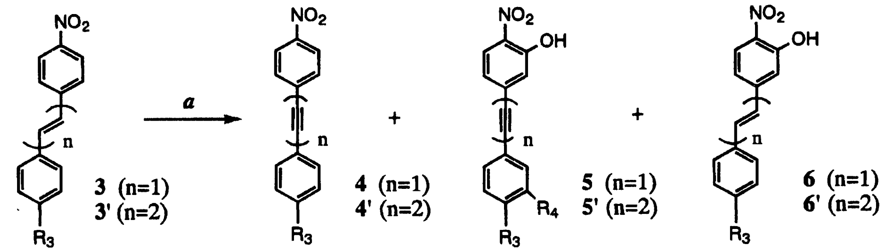
Table 1. Compound Numbers (**1**—**10**) and Their Substituents



i)

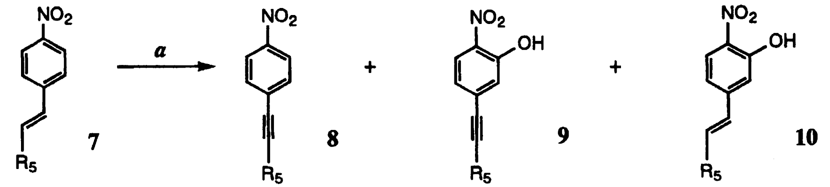
1	2	R_1	R_2
1a	**2a**	H	H
1b	**2b**	Me	Me
1c	**2c**	MeO	MeO
1d	**2d**	Cl	Cl
1e	**2e**	Et_2N	Et_2N
1f	**2f**	CN	CN
1g	**2g**	NO_2	MeO

ii)



3	3′	4	4′	R_3	5	R_3	R_4	5′	R_3	R_4	6	6′	R_3
3a	—	**4a**	—	Ph_2N	**5a**	Ph_2N	H	—	—	—	**6a**	—	Ph_2N
3b	—	**4b**	—	Et_2N	**5b**	Et_2N	H	—	—	—	**6b**	—	Et_2N
3c	**3′c**	**4c**	**4′c**	Me_2N	**5c**	Me_2N	H	**5′c**	Me_2N	H	—	**6′c**	Me_2N
3d	**3′d**	**4d**	**4′d**	MeO	**5d**	MeO	H	**5′d**	MeO	H	**6d**	**6′d**	MeO
3e	**3′e**	**4e**	**4′e**	H	**5e**	H	H	**5′e**	H	H	—	**6′e**	H
3f	**3′f**	**4f**	—	NO_2	**5f**	NO_2	OH	—	—	—	—	—	—
3g	—	—	—	Br	**5g**	Br	H	—	—	—	—	—	—

iii)



a: *t*-BuOK/DMF in the air

7	8	9	10	R_5
7h	**8h**	**9h**	—	9-Anthryl
7i	—	**9i**	**10i**	1-Anthryl
7j	—	**9j**	—	4-Pyridyl
7k	—	**9k**	—	3,4-Methylene-Dioxyphenyl
7l	—	**9l**[a]	—	3-Nitrophenyl

a) Obtained as 3,4′-dihydroxy-3′,4-dinitrodiphenylacetylene.

species expected was proved to explain the mechanism of this dehydrogenation reaction. In connection with ESR studies, cyclic voltammetric measurements of **3** and **4** were carried out.

Results and Discussion

Two One-Stage Conversion Reactions: Dehydrogenation and Hydroxylation.[5] **(i) 9,10-Bis-(4-substituted styryl)anthracenes (1) Series.** In the course of the development of new fluorescent and/or chemiluminescent probes for analytical and/or biological studies, we have found that aromatic acetylenic compounds were directly obtained from the corresponding ethylenic compounds without proceeding through the usual halogenation–dehydrogenation process. Compounds **1a**—**g** synthesized by the Wittig–Horner reaction were treated by the orthodox method to obtain the corresponding acetylenes (**2a**—**g**). However, **2e**—**g**

were not obtained, because a bromination reaction did not proceed from the corresponding alkenes. Luckily, we have found that **2e**—**g** could be obtained at room temperature from **1e**—**g** by treatment with a large excess of *t*-BuOK in DMF in the air. As attempts to get **2a**—**d** from **1a**—**d** have been impossible, we suppose that the presence of such substituents leads to electronic perturbation on both benzene rings. For examination of the novel one-stage direct conversion reaction of an ethylenic bond into an acetylenic bond, we chose a *p*-nitrostyryl system (**3**) and explored the scope and the limitation of this process.

(ii) *p*-Substituted *p*′-Nitrostilbenes (3) and 1-(*p*-Nitrophenyl)-4-(*p*-substituted phenyl)-1,3-butadienes (3′) Series. These olefins (**3a**—**g** and **3′c**—**f**) were easily synthesized by the reaction of diethyl *p*-nitrobenzylphosphonate with the corresponding aldehydes in the presence of NaOMe in EtOH or EtOH–DMF. Basically, compounds (**3a**—**g**) were converted into the corresponding acetylenes (**4**) by treatment with an excess of *t*-BuOK (**3** : *t*-BuOK=1 : 4) in DMF in the air. Other bases (NaH, NaOH, NaOMe, Et_3N, and KOH) and solvents (DMSO, THF, benzene, and EtOH) were used to check whether the reaction takes place or not; it was found that the combination of *t*-BuOK and DMF or DMSO was essential. Interestingly, the reaction hardly occurred at all in DMF degassed with nitrogen, but proceeded smoothly by bubbling oxygen into the above mixture. Consequently, oxygen participates essentially in the triple bond formation. Compounds **3b**—**f** could be converted into acetylenes **4b**—**f**. However, under the reaction conditions, *trans*-stilbene was stable and completely recovered. So we supposed that the presence of a strong electron-attracting substituent such as a nitro group was necessary on a benzene ring.

Unexpectedly, we found that the use of a larger excess of *t*-BuOK gave the hydroxy compounds (**5a**—**g**). The dinitro compound **3f** gave easily the bisphenol **5f**, besides **4f**, under the above condition. As the first example of a direct hydroxylation into a benzene ring, the formation of 2-nitrophenol by treatment of nitrobenzene with KOH is known.[6] In addition, Guthrie and Nutter have proposed a possible mechanism for a similar hydroxylation reaction of nitrobenzene with *t*-BuOK in THF.[7] Otherwise, it is very interesting that formation of **6a**, **6b**, and **6d** from the corresponding **3** were observed by a direct hydroxylation reaction which seemed to be earlier than a dehydrogenation of the ethylenic bond according to conditions. The electronic effects of the substituent on the benzene nucleus seem to influence both the oxidative dehydrogenation of the CH=CH bond to the triple bond and that of the succeeding and/or preceding hydroxylation into the ortho position of a nitro group on the benzene nucleus.

Several interesting facts have recently been found, i.e., the conversion of compounds **3′**, which is the vinylog of **3**, to the phenols (**5′c**—**e**, and **6′c**—**e**),[8] the direct hydroxylation of **4** to **5**, and the conversion of 4,4′-dinitrobibenzyl and 4-nitrotoluene to **3**, **4**, and **5**.[9] These results are being clarified by high performance liquid chromatographic (HPLC) analyses of the reaction products; the details will be reported in the near future. The expecting diynes (**4′c**—**e**) seemed to be a transient species and then resisted to be isolated because of a trace amount. The direct conversion of a diene to a diyne is unique if it is restrictive.

(iii) *p*-Nitrostyryl Derivatives (7) Series. According to the same procedure as the series of **3**, compounds (**7h**—**l**) were prepared. As in the previous section, the use of a large excess of *t*-BuOK gave mainly the hydroxy compounds (**9**). In the series **8** and **10**, we could only isolate **8h** and **10i**. The separation of the many other kinds of compounds expected to be produced in the reaction was very difficult even by using a flash silica-gel column chromatography. Compounds **3**—**10** are expected to be of particular interest in the field of new functional materials such as non-linear optical materials and reagents for analysis with UV-vis and FL properties.[10]

UV-vis and FL Spectral Properties. Table 2 summarizes the absorption spectral data of the longest

Table 2. Electronic Spectral Data of Compounds **1**—**9**

Compound	λ_{max}/nm ($\varepsilon \times 10^{-1}$)		
	Benzene	Ethanol	Methanol
3a	431 (3.13)	422 (2.88)	
3b	443 (3.15)	441 (3.08)	440 (2.77)
3c	431 (2.28)	429 (1.61)	427 (1.29)
3d	375 (2.52)	373 (3.19)	371 (2.85)
3e	352 (2.47)	343 (1.73)	347 (2.45)
3e	447 (3.68)	439 (1.42)	
3′c	447 (3.68)	439 (1.42)	
3′d	399 (3.43)	395 (3.85)	
3′e	381 (3.51)	376 (3.71)	
4b	418 (2.36)	416 (2.51)	414 (2.39)
4c	409 (2.28)	405 (2.27)	403 (2.27)
4d	353 (2.25)	350 (2.37)	349 (2.45)
4e	329 (2.17)	325 (2.42)	325 (2.47)
5a	435 (2.47)	409 (2.22)	
5b	448 (2.72)	432 (2.38)	429 (2.38)
5c	435 (2.44)	418 (2.09)	415 (2.14)
5d	380 (2.50)	368 (1.04)	365 (2.76)
5e	352 (2.47)	342 (1.69)	338 (1.87)
5′c	440 (2.30)	412 (2.14)	
5′d	384 (3.49)	367 (2.39)	
6b	468 (1.64)	458 (2.59)	454 (2.48)
6′c	474 (3.59)	459 (2.29)	
6′d	422 (3.56)	412 (3.72)	
6′e	404 (3.62)	394 (3.52)	
7h	413 (1.58)	403 (1.29)	
7i	412 (1.78)	409 (1.83)	
7k	336 (2.66)	331 (2.71)	
8h	442 (1.80)	435 (1.67)	
9h	441 (1.75)	408 (3.53)	
9i	418 (1.69)	429 (0.72)	

wavelength maxima of compounds **3**—**9**. From these results, it was apparent in a ii) series that polar solvents bring about a red shift which decreased as the order is $Et_2N>Me_2N>Ph_2N>MeO>H$, and the order of when restriction on the same substituent is 6>3>5>4. The spectra of the acetylenic phenols in a phosphate buffer solution (0.1 M Na_2HPO_4–0.1 M NaOH, pH 12/EtOH=9/1) were measured (1 M=1 mol dm^{-3}): the longest wavelengths (ε_{max}/nm×10^{-4}) were **5b**, 426 (2.21); **5c**, 413 (1.08); **5d**, 343 (1.36); **9h**, 435 (0.76); **9k**, 422 (0.82). Contrary to our expectation, the phenolates showed a blue shift and a hypochromic effect to the corresponding phenols in organic solvents (Table 2). In Table 3, the FL data [excitation and emission maxima, relative fluorescence intensity (RFI) and Stokes' shift] of the compounds studied are summarized. The excitation and emission maxima of these compounds showed at 350—470 nm and 440—580 nm, respectively. Stokes' shifts of 60—170 nm were observed; apparently the electronic character of the substituents seems to reflect these results, especially in push–pull type systems. As regard RFI-values, a larger solvent effect was observed in benzene than in ethanol. It is remarkable that the push–pull diphenylbutadiene **3′c** has the largest RFI among them, which will be expected for an FL reagent for analysis of enzymes; esters of fatty acids with compound **3′** can be a candidate for enzyme substrates.

Reaction Mechanism of a Novel One-Stage Conversion of the CH=CH Bond to the C≡C Bond. In order to gain insight into the mechanism of this conversion a detailed investigation of the reaction of stilbene **3b** with *t*-BuOK in DMF to give acetylene **4b** was carried out employing optical absorption, ESR, and HPLC-CL[11] to analyze the process of the reaction. The radical anion of **3b** (denoted as **3b**$^{\bullet-}$) or [**4b**]$^{\bullet-}$ could be traced as a transient intermediate. Based on these findings, a possible mechanism for the dehydrogenation of compounds **3** to afford acetylenes is proposed as shown in Scheme 1

Optical absorption and ESR measurements were carried out for the reaction system composed of a DMF solution of **3b** (0.15 mM, 2.0 ml) and *t*-BuOK (20 mg) in the air. The optical absorption spectra observed just after an addition of *t*-BuOK showed an identical absorption spectra to **3b**, as shown in Fig. 1-a. After sealing with a tap during 10 min, the color of the solution gradually changed to dark green, as characterized by absorption maxima at 410, 450 (sh), 588, and 665 nm, as shown in Fig. 1-b. The ESR spectrum recorded for the solution (inset of Fig. 1) revealed the presence of a free radical species ($g=2.004$), having a well resolved hyperfine structure (hfs). After briefly bubbling oxygen gas into the mixture, we found that the ESR signal of the radical species had completely disappeared, and the color of the solution quickly turned to orange, as shown by the absorption maximum at 455 nm arose from **3b**. When the atmosphere was changed to nitrogen, the color of the solution returned to dark green and the identical optical absorption and the ESR signal were again observed. Finally, the color of the solution changed to orange-red with absorption maxima at 377 and 407 nm (Fig. 1-c), about 40 min. after addition of *t*-BuOK under aerobic conditions. At longer exposure times the color turned to dark green and the ESR signal of the free radical species was not detected, even after nitrogen gas was bubbled into the mixture. The observed optical parameters were consistent with those of the reaction product **4b**, suggesting that the conversion reaction of **3b** to **4b** was completed. For the analysis of this reaction process, normal phase HPLC measurements with ultraviolet detection were preliminarily carried out to show that the increase of the peak due to **4b** corresponded with the decrease of **3b** with time. These observations indicate that the paramagnetic dark green substance, as characterized by absorption maxima at 410, 450 (sh), 588, and 665 nm, could be one of the transient intermediate species involved in the present reaction system. In addition, the intermediate species must have a very short life-time in the presence of molecular oxygen.

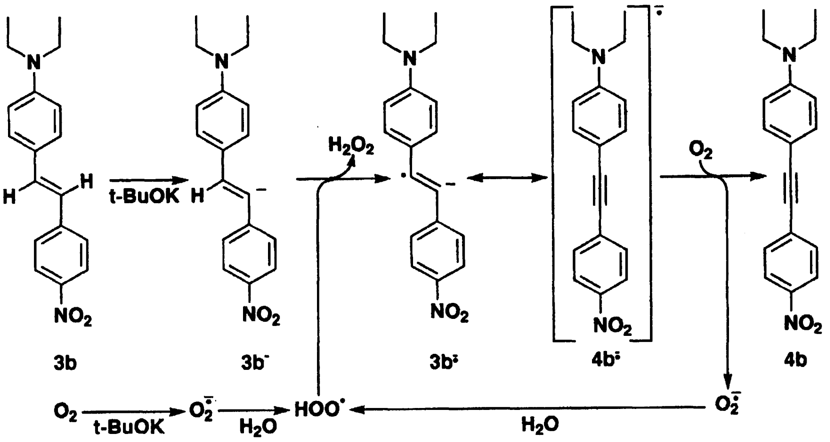
Computer simulation of the ESR spectrum using the observed hfs of the radical species showed that the spectrum consisted of the three sets of triplet splittings derived from one nitrogen atom ($a^N=8.20$ gauss) and from two sets of two equivalent protons ($a^H=3.23$ gauss and $a^H=1.08$ gauss). The contribution of a doublet splitting due to the ethylenic protons was not observed. From a comparison of the estimated hyperfine coupling constants (hfcc) and those of a numerical ESR parameters of nitrobenzene radicals, we found that the hfcc were similar to the anion radicals of *p*-substituted nitrobenzene derivatives, such as *p*-nitrobiphenyl anion radical ($a^N=9.70$, $a^H=3.30$, and $a^H=1.07$ gauss).[12] Furthermore, the observed hfcc were in excellent agreement with the prediction of McLachlan MO calculation[13] performed for **4b**$^{\bullet-}$. Further efforts were made to understand the electronic structure of the radical species, with the aid of electrochemical techniques coupled with optical absorption and ESR measurements. By using an optically transparent thin-layer electrode,[14] the optical spectra generated on reduction of **4b** were measured at room temperature. The observed spectra (Fig. 2-a) gave absorption maxima at 412, 453, 586, and 663 nm, which were similar to those of the dark green solution (Fig. 1-b; 410, 450 (sh), 588, and 665 nm). A simultaneous electrochemical-ESR spectrum[15] observed for one-electron reduced species of **4b** (inset of Fig. 2) revealed the identical hfs ($a^N=8.20$, $a^H=3.20$, and $a^H=1.10$ gauss) to that recorded for the dark-green reaction mixture (inset of Fig. 1).

These observations provide strong experimental evidence that an anion radical [**4b**]$^{\bullet-}$ is the intermediate species in the present dehydrogenation reaction.

Table 3. Fluorescence Spectral Data of **3**—**9**[a)]

	λ_{ex}/nm	λ_{em}/nm	λ_{ex}/nm	λ_{em}/nm	$(\lambda_{em}-\lambda_{ex})$/nm	
Compound	Benzene	Ethanol	Benzene	Ethanol	Benzene	Ethanol
3a	430	420	540 (45.42)	560 (0.026)	110	140
3b	450	420	570 (29.01)	570 (0.013)	120	150
3c	430	420	570 (21.98)	560 (0.013)	140	140
3d	390	400	480 (0.13)	540 (0.078)	90	140
3e	N.D.	400	N.D.[b)]	520 (0.016)	—	120
3′c	470	420	570 (148.4)	570 (0.0059)	100	150
3′d	400	420	570 (59.35)	440 (0.044)	170	120
3′e	420	410	480 (1.70)	560 (0.085)	60	150
4b	420	420	550 (11.53)	540 (0.008)	130	120
4c	470	400	550	540 (0.005)	80	140
4d	N.D.	390	N.D.	510 (0.010)	—	120
5a	440	N.D.	570 (4.32)	N.D.	—	130
5b	470	400	580 (0.22)	540 (0.0037)	110	130
5c	400	410	560 (0.35)	540 (0.0015)	160	130
5d	N.D.	N.D.	N.D.	N.D.	—	—
5e	N.D.	N.D.	N.D.	N.D.	—	—
5′c	470	400	610 (9.34)	570 (0.016)	140	170
5′d	440	350	540 (0.16)	450 (0.0029)	100	100
6b	480	420	590 (1.49)	570 (0.0037)	110	150
6′c	470	400	610 (9.34)	570 (0.006)	140	170
6′d	450	450	540 (7.91)	570 (0.016)	90	120
6′e	420	450	480 (0.002)	570 (0.016)	60	140
7h	420		510 (30.76)		90	
7i	420		510 (100.00)		90	
8h	420	N.D.	510 (43.96)	N.D.	90	—
9h	450		550 (9.23)		100	
9i	430		550 (2.27)		120	

a) Values in parenthesis indicate relative fluorescence intensities (RFI); the RFI of **7i** in benzene was arbitrarily taken as 100. b) N.D. : Non-detectable.



Scheme 1.

In comparison of the one-electron reduction potentials of **4b** to $\mathbf{4b}^{\bullet-}$ [−1434 mV (vs. Ag/Ag$^+$)] and that of molecular oxygen to superoxide anion radical ($O_2{}^{\bullet-}$), which was well established to be about −1100 mV (vs. Ag/Ag$^+$), we found that the $\mathbf{4b}^{\bullet-}$ anion radical species can be readily oxidized to **4b** by the reaction with oxygen. In fact, the ESR signal due to the intermediate species ($\mathbf{4b}^{\bullet-}$) was completely disappeared after briefly oxygen gas ($g_{//}=2.080$ and $g_{\perp}=2.008$)[16)] was clearly observed for the frozen solution. The origin of $O_2{}^{\bullet-}$ was thought to be derived from atmospheric oxygen. This is the reason why the suspension of *t*-BuOK in well degassed DMF gave no detectable ESR signals of $O_2{}^{\bullet-}$. When **3b** was added to the above suspension, the ESR signal of $O_2{}^{\bullet-}$ completely disappeared. In this case, however, the rapid formation of hydrogen peroxide was clearly detected by HPLC with CL detection.[11)] By combining the results of the ESR and HPLC measurements, we found that the molecular oxygen was converted to hydrogen peroxide after the two-electron re-

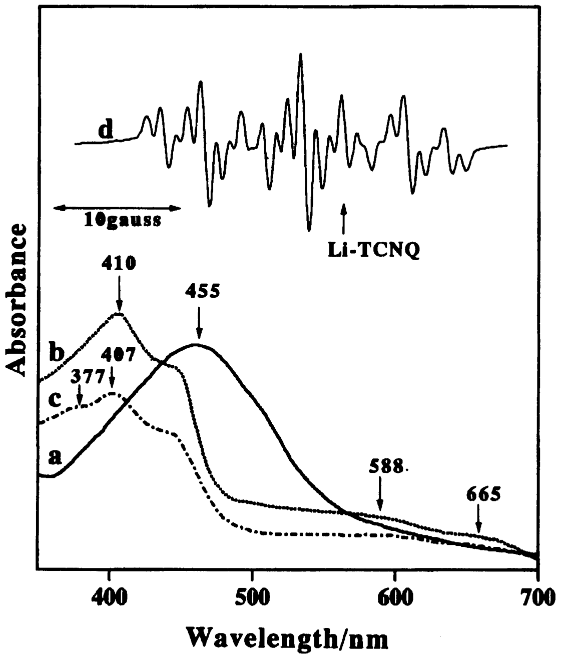


Fig. 1. Optical absorption spectra observed for the DMF solution of **3b** (0.15 mM, 2.0 ml); a) Spectra recorded just after addition of *t*-BuOK (20 mg) under pressure; b) Spectra observed for the same solution after sealing with a septum during 10 min.; c) Spectra recorded for the solution after 40 min. on addition of *t*-BuOK. Inset; ESR spectrum recorded at 25 °C for the same solution of b). Li-TCNQ (Li salt of tetracyanoquinodimethane) was used as an external standard for *g*-value (g=2.0025).

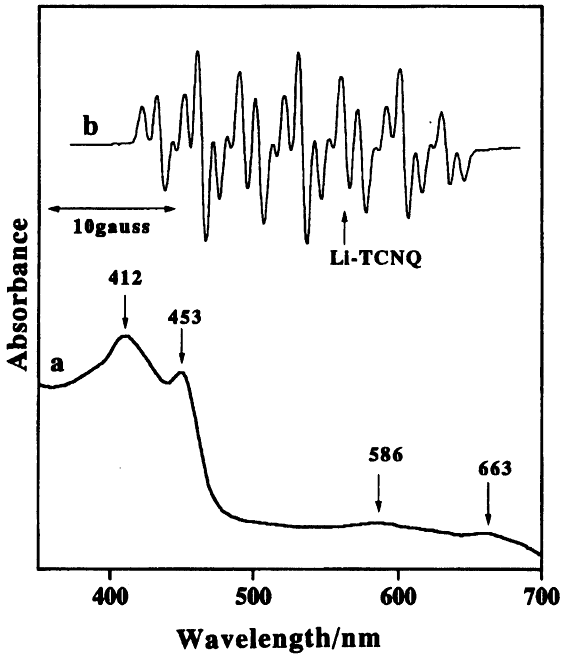


Fig. 2. Electrochemical optical absorption spectra observed for the DMF solution of **4b** (1.0 mM) in the presence of TBAP (0.1 M) under nitrogen at 25 °C. Applied potential is adjusted at −1500 mV vs. (Ag/Ag$^+$). Inset; ESR spectrum recorded for **4b** using electrochemical ESR cell at 25 °C in vacuo, after supplying −1500 mV vs. (Ag/Ag$^+$).

duction processes. The oxidizing reagent in the present system is, therefore, concluded to be the molecular oxygen.

This reaction was completely inhibited when a DMF solution of **3b** was treated with *t*-BuOK under vacuum. We found that an atmosphere of oxygen is also indispensable in the conversion reaction of **3b** to **4b**.

It is noted here that the yield of the reaction product **4b** markedly diminished when the solvent was thoroughly dry DMF distilled twice over CaH_2, but also when moist DMF was used instead of a fresh bottle of reagent grade. This suggests that trace amounts of water were necessary in this reaction. Knowing the requirement of water for the reaction to proceed, a mechanism for the one-stage conversion is proposed, as illustrated in Scheme 1. In the first reaction stage, *t*-BuOK is expected to abstract or at least to promote the abstraction of an ethylenic proton from **3b** to give the anion (**3b**$^-$). Then hydroperoxyl radical, derived from the reaction between $O_2^{\bullet -}$ and water, abstracts an olefinic hydrogen atom perturbed significantly by a nitro group in **3b**$^-$ to give **3b**$^{\bullet -}$ and the hydroperoxyl radical reduces to hydrogen peroxide. The anion radical **3b**$^{\bullet -}$, bearing a carbon–carbon double bond, is isoelectronic and resonant with the anion radical of a diphenylacetylene derivative ([**4b**]$^{\bullet -}$), which corresponds to the intermediate observed by ESR and by optical absorption measurements, as described earlier. The one-electron transfer from [**4b**]$^{\bullet -}$ to molecular oxygen gives **4b** and $O_2^{\bullet -}$ which reacts with water. Consequently, **3b** is oxidized to **4b**, concomitant with a two-electron reduction of molecular oxygen to hydrogen peroxide (Scheme 1). Attempts to measure the ^{1}H NMR of **3b**$^-$ and that after subsequent treatment with D_2O were unsuccessful, perhaps because of its short lifetime. However, an increase of about 10% was observed in the relative ratio $[(M^+ + 1)/M^+]$ of **3b** with the corresponding peaks of the mono-deuterated compound, which suggests the existence of some **3b**$^-$. We are now exploring more details of the direct hydroxylation reaction.

Experimental

Melting points were measured on a Yanagimoto MP-35 melting point apparatus and are uncorrected. UV-vis spectra were recorded on a Shimadzu UV-250F and a Hitachi UV-250 spectrometer, IR spectra on a JASCO 810 spectrophotometer, ^{1}H NMR spectra in $CDCl_3$ solution on a JEOL FX-90Q or a JEOL JNM-GX-400 spectrometer with Me_4Si as the internal standard (J values are given in Hz), and mass spectra on a JEOL JMS-DX 303 instrument. Fluorescence spectra were recorded on a Hitachi 650-10S fluorescence spectrophotometer.

Synthesis of Styryl and Butadienyl Compounds (3, 3′, and 7). A typical procedure for the preparation of

3a is as follows: A mixture of diethyl *p*-nitrobenzylphosphonate (5.47 g, 0.02 mol) and *p*-diphenylaminobenzaldehyde (5.47 g, 0.02 mol) was stirred in the presence of NaOEt (Na, 0.70 g, 0.03 mol) in EtOH (40 ml)–DMF (40 ml) at room temperature for 3 h. The precipitate which deposited was filtered off, washed with EtOH, and then recrystallized from benzene (yield, 7.50 g, 95%). Orange crystals; mp 145—146 °C; Found: C, 79.44; H, 5.29; N, 7.14%. Calcd for $C_{26}H_{20}N_2O_2$: C, 79.57; H, 5.14; N, 7.14%.

3b: Yield: 90%; red crystals; mp 177—179 °C. Found: C, 72.62; H, 6.86; N, 9.41%. Calcd for $C_{16}H_{20}N_2O_2$: C, 72.95; H, 6.80; N, 9.45%.

3c: 63%; red crystals; mp 249—251 °C. Found: 71.66; H, 6.07; N, 10.42%. Calcd for $C_{16}H_{16}N_2O_2$: C, 71.62; H, 6.01; N, 10.44%.

3d: 80%; yellow crystals; mp 129—121 °C. Found: C, 70.55; H, 5.14; N, 5.44%. Calcd for $C_{15}H_{13}NO_3$: C, 70.57; H, 5.13; N, 5.49%.

3e: 80%; yellow crystals; mp 154—156 °C. Found: C, 74.61; H, 5.02; N, 6.26%. Calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22%.

3f: 88%; yellow crystals; mp 292—295 °C. Found: C, 62.13; H, 3.78; N, 10.29%. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37%.

3g: 68%; yellow crystals; mp 198—200 °C. Found: C, 55.25; H, 3.37; N, 4.58%. Calcd for $C_{14}H_{10}NO_2Br$: C, 55.29; H, 3.31; N, 4.61%.

A series of **3′** and **7** were prepared according to the above method from the phosphonate and the corresponding aldehydes. Yields were not always obtained under the best conditions.

3′c: 48%; red crystals; mp 262—264 °C. Found: C, 73.62; H, 6.23; N, 9.37%. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.45; H, 6.16; N, 9.52%.

3′d: 49%; orange crystals; mp 169—171 °C. Found: C, 72.55; H, 5.43; N, 5.02%. Calcd for $C_{17}H_{15}NO_3$: C, 72.59; H, 5.38; N, 4.98%.

3′e: 52%; yellow crystals; mp 172—175 °C. Found: C, 76.54; H, 5.31; N, 5.56%. Calcd for $C_{16}H_{13}NO_2$: C, 76.47; H, 5.22; N, 5.58%.

3′f: 84%; orange crystals; mp 262—264 °C. Found: C, 64.89; H, 4.15; N, 9.42%. Calcd for $C_{16}H_{12}N_2O_4$: C, 64.86; H, 4.08; N, 9.46%.

7h: 74%; orange crystals; mp 222—224 °C. Found: 81.47; H, 4.83; N, 4.25%. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31%.

7i: 68%; orange crystals; mp 199—201 °C. Found: C, 81.10; H, 4.76; N, 4.28%. Calcd for $C_{22}H_{15}NO_2$: C, 81.21; H, 4.65; N, 4.31%

7j: 62%; pale yellow crystals; mp 163—165 °C. Found: C, 69.06; H, 4.55; N, 12.44%. Calcd for $C_{13}H_{10}N_2O$: C, 69.01; H, 4.46; N, 12.39%

7k: 67%; yellow crystals; mp 188—190 °C. Found: C, 67.04; H, 4.20; N, 5.19%. Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20%.

7l: 89%; yellow crystals; 220—224 °C. Found: 62.19; H, 3.83; N, 10.42%. Calcd for $C_{14}H_{10}N_2O_4$: C, 62.22; H, 3.73; N, 10.37%.

Reaction of 3, 3′, and 7 with *t*-BuOK in DMF in the Air Typical reaction conditions for **3d** to get the phenol **5d** preferentially are as follows: Into a solution of **3d** (0.20 g, 0.78 mmol) in DMF (50 ml) a large excess of *t*-BuOK (1.32 g, 12 mmol) was added at once and this mixture was stirred in the air at room temperature for 90 min. The reaction mixture was poured into water (200 ml) and mixed with HCl (2 M, 60 ml). The organic layer was extracted with benzene (100 ml×2) and washed with NaOH (2 M, 60 ml). The alkaline water layer was neutralized with HCl, extracted with benzene (50 ml×4), and the benzene layer was dried with $MgSO_4$. Evaporation of the extract resulted in brownish-yellow crystals, which were recrystallized from EtOH to give pure compound **5d** in the yield of 43%. The first organic layer after alkali washing was concentrated to give a trace amount of **4d**, which was successfully obtained from **3d** by a change of mole ratio (**3d**:*t*-BuOK=1:4) under similar conditions in a 39% yield after purification with silica-gel column chromatography. In the case of lager mole ratio (1:15), **6d** was isolated.

4a: This compound could not be isolated, perhaps because of the succeeding rapid hydroxylation.

4b: 50%; dark red crystals; mp 164—167 °C EI-MS (m/z) 294 (M^+); IR (Nujol) 2200 (C≡C). Found: C, 73.38; H, 6.26; N, 9.32%. Calcd for $C_{18}H_{18}N_2O_2$: C, 73.44; H, 6.16; N, 9.52%. ^{1}H NMR δ=1.19 (6H, t, J=7.1 Hz, CH_3), 3.40 (4H, q, J=7.1 Hz, CH_2), 6.63 (2H, d, J=9.1 Hz, ArH), 7.40 (2H, d, J=9.1 Hz, ArH), 7.59 (2H, d, J=9.0 Hz, ArH), 8.18 (2H, d, J=9.0 Hz, ArH).

4c: 53%; reddish brown crystals; mp 218—220 °C; EI-MS (m/z) 266 (M^+); IR 2210 (C≡C). Found: C, 71.90; H, 5.45; N, 10.45%. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52%. ^{1}H NMR δ=3.02 (6H, s, NMe_2), 6.67 (2H, d, J=7.0 Hz), 7.43 (2H, d, J=7.0 Hz, ArH), 7.59 (2H, d, J=8.9 Hz, ArH), 8.18 (2H, d, J=8.9 Hz, ArH).

4d: 10%; yellow crystals; mp 118—120 °C; EI-MS (m/z) 253 (M^+); IR 2210 (C≡C). Found: C, 71.24; H, 4.61; N, 5.51%. Calcd for $C_{15}H_{11}NO_3$: C, 71.14; H, 4.38; N, 5.53%. ^{1}H NMR δ=3.85 (3H, s, OMe), 6.91 (2H, d, J=8.8 Hz, ArH), 7.50 (2H, d, J=8.8 Hz, ArH), 7.63 (2H, d, J=8.8 Hz, ArH), 8.20 (2H, d, J=8.8 Hz, ArH).

4e: 8%: yellow crystals; mp 113—115 °C; EI-MS (m/z) 223 (M^+); IR 2210 (C≡C). Found: C, 75.94; H, 4.29; N, 6.29%. Calcd for $C_{14}H_9NO_2$: C, 75.32; H, 4.06; N, 6.28%. ^{1}H NMR δ=7.39—7.41 (3H, m, ArH), 7.55—7.58 (2H, m, ArH), 7.67 (2H, d, J=9.0, ArH), 8.23 (2H, d, J=8.9, ArH).

4f: 8%; pale yellow crystals; mp 205—207 °C; EI-MS (m/z) 268 (M^+); IR 2210 (C≡C). Found: C, 62.58; H, 3.25; N, 10.35%. Calcd for $C_{14}H_8N_2O_4$: C, 62.69; H, 3.01; N, 10.45%. ^{1}H NMR δ=7.72 (4H, d, J=8.8 Hz, ArH), 8.27 (4H, d, J=8.8 Hz, ArH).

5a: 22%; red plates; mp 135—137 °C; EI-MS (m/z) 406 (M^+); IR 2200 (C≡C). Found: C, 76.80; H, 4.58; N, 6.85%. Calcd for $C_{26}H_{18}N_2O_3$: C, 76.83; H, 4.46; N, 6.89%. ^{1}H NMR δ=7.00 (2H, d, J=8.8 Hz, ArH), 7.07 (1H, dd, J=1.5 and 8.8 Hz, ArH), 7.12 (5H, m, ArH), 7.25 (1H, d, J=1.5 Hz, ArH), 7.30 (5H, m, ArH), 7.38 (2H, d, J=8.8 Hz, ArH), 8.07 (1H, d, J=8.8 Hz, ArH), 10.65 (1H, s, OH).

5b: 48%: dark red crystals; mp 149—151 °C EI-MS (m/z) 310 (M^+); IR 2200 (C≡C). Found: C, 69.66; H, 5.84; N, 8.98%. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03%. ^{1}H NMR δ=1.19 (6H, t, J=7.1 Hz, CH_3), 3.40 (4H, q, J=7.1 Hz, CH_2), 6.60 (2H, d, J=8.8 Hz, ArH), 7.00 (1H, dd, J=1.5 and 8.8 Hz, ArH), 7.20 (1H, d, J=1.5 Hz, ArH), 7.40 (2H, d, J=8.8 Hz, ArH), 8.00 (1H, d, J=8.8, Hz, ArH), 10.70 (1H, s, OH).

5c: 39%; red crystals; mp 197—200 °C; EI-MS (m/z) 282 (M^+); IR 2200 ($C\equiv C$). Found: C, 68.20; H, 5.16; N, 9.92%. Calcd for $C_{16}H_{14}N_2O_3$: C, 68.07; H, 5.00; N, 9.93%. ^{1}H NMR δ=3.02 (6H, s, NMe$_2$), 6.66 (2H, d, J=8.8 Hz, ArH), 7.04 (2H, dd, J=1.8 and 8.8 Hz, ArH), 7.21 (1H, d, J=1.8, ArH), 7.42 (2H, d, J=8.8 Hz, ArH), 8.03 (1H, d, J=8.8 Hz, ArH), 10.66 (1H, s, OH).

5d: 43%; yellow crystals; mp 167—169 °C; EI-MS (m/z) 269 (M^+); IR 2200 ($C\equiv C$). Found: C, 67.00; H, 4.28; N, 5.15%. Calcd for $C_{15}H_{11}NO_4$: C, 66.91; H, 4.12; N, 5.20%. ^{1}H NMR δ=3.85 (3H, s, MeO), 6.91 (2H, d, J=9.5 Hz, ArH), 7.07 (1H, dd, J=8.8 and 1.8 Hz), 7.26 (1H, d, J=1.8 Hz, ArH), 7.49 (2H, d, J=9.5 Hz, ArH), 8.07 (1H, J=8.8 Hz, ArH), 10.64 (1H, s, OH).

5e: 8%; yellow crystals; mp 123—125 °C; EI-MS (m/z) 239 (M^+); IR 2200 ($C\equiv C$). Found: C, 70.18; H, 3.98; N, 5.85%. Calcd for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.86%. ^{1}H NMR δ=7.11 (1H, dd, J=1.5 and 8.8 Hz, ArH), 7.30 (1H, d, J=1.5 Hz, ArH), 7.40 (3H, m, ArH), 7.56 (2H, m, ArH), 8.09 (1H, d, J=8.8 Hz, ArH), 10.63 (1H, s, OH).

5f: 8%; red crystals; mp 250—252 °C; EI-MS (m/z) 300 (M^+); IR 2200 ($C\equiv C$). Found: C, 56.09; H, 2.89; N, 9.25%. Calcd for $C_{14}H_8N_2O_6$: C, 56.00; H, 2.69; N, 9.33%. ^{1}H NMR δ=7.14 (2H, dd, J=1.5 and 8.8 Hz, ArH), 7.34 (2H, d, J=1.5 Hz, ArH), 8.13 (2H, d, J=8.8 Hz, ArH), 10.62 (2H, s, OH).

5g: 22%; orange crystals; mp 173—175 °C; EI-MS (m/z) 317 (M^+); IR 2200 ($C\equiv C$). Found: C, 52.95; H, 2.69; N, 4.44%. Calcd for $C_{14}H_8N_2O_3Br$: C, 52.85; H, 2.53; N, 4.40%. ^{1}H NMR δ=7.05 (1H, dd, J=2.0 and 8.8 Hz, ArH), 7.29 (1H, d, J=2.0 Hz, ArH), 7.41 (2H, m, ArH), 7.53 (2H, m, ArH), 8.09 (1H, d, J=8.8 Hz, ArH), 10.61 (1H, s, OH).

5′c: 13%; dark red crystals; mp 181—184 °C, EI-MS (m/z) 306 (M^+); IR 2200 ($C\equiv C$). Found: C, 70.53; H, 4.70; N, 9.15%. Calcd for $C_{18}H_{14}N_2O_3$: C, 70.58; H, 4.61; N, 9.15%. ^{1}H NMR δ=3.01 (6H, s, NMe), 6.62 (2H, d, J=9.0 Hz, ArH), 7.05 (1H, dd, J=1.5 and 8.8 Hz, ArH), 7.24 (1H, d, J=1.5 Hz, ArH), 7.42 (2H, d, J=9.0 Hz, ArH), 8.05 (1H, d, J=8.8 Hz, ArH), 10.61 (1H, s, OH).

5′d: 8%; yellow needles; mp 207—210 °C; EI-MS (m/z) 293 (M^+); IR 2200 ($C\equiv C$). Found: C, 69.70; H, 4.02; N, 4.79%. Calcd for $C_{17}H_{11}NO_4$: C, 69.62; H, 3.79; N, 4.78%. ^{1}H NMR δ=3.84 (3H, s, MeO), 6.87 (2H, d, J=8.8 Hz, ArH), 7.07 (1H, dd, J=1.8 and 8.8 Hz), 7.26 (1H, d, J=1.8 Hz, ArH), 7.49 (2H, d, J=9.5 Hz, ArH), 8.07 (1H, d, J=8.8 Hz, ArH), 10.64 (1H, s, OH).

5′e: 8%: yellow crystals; mp 162—165 °C; EI-MS (m/z) 263 (M^+); IR 2200 ($C\equiv C$). Found: C, 72.58; H, 3.65; N, 5.22%. Calcd for $C_{16}H_9NO_3$: C, 73.00; H, 3.45; N, 5.32%. ^{1}H NMR δ=7.09 (1H, dd, J=1.5 and 8.8 Hz, ArH), 7.29 (1H, d, J=1.5 Hz, ArH), 7.35—7.44 (3H, m, ArH), 7.54—7.56 (2H, m, ArH), 8.21 (1H, d, J=8.8 Hz, ArH), 10.63 (1H, s, OH).

6a: 25%; red crystals; mp 162—164 °C; EI-MS (m/z) 408 (M^+). Found: C, 76.38; H, 5.01; N, 6.82%. Calcd for $C_{26}H_{20}N_2O_3$: C, 76.45: H, 4.94; N, 6.86%. ^{1}H NMR δ=6.91 (1H, d, J=16.0 Hz, CH=CH), 7.05 (2H, d, J=8.3 Hz, ArH), 7.08—7.14 (7H, m, ArH), 7.17 (1H, d, J=1.5 Hz, ArH), 7.22 (1H, d, J=16.0 Hz, CH=CH), 7.26—7.31 (4H, m, ArH), 7.40 (2H, d, J=8.3, ArH), 8.06 (1H, d, J=9.3 Hz, ArH), 10.75 (1H, s, OH).

6b: 11%; red crystals; mp 137—139°C; EI-MS (m/z) 312 (M^+). Found: C, 69.10; H, 6.48; N, 8.91%. Calcd for $C_{18}H_{20}N_2O_3$: C, 69.21; H, 6.45; N, 8.97%. ^{1}H NMR δ=1.20 (6H, t, J=7.1 Hz, CH$_3$), 3.41 (4H, q, J=7.1 Hz, CH$_2$), 6.67 (2H, d, J=9.2 Hz, ArH), 6.80 (1H, d, J=16.1 Hz, CH=CH), 7.01 (1H, dd, J=2.0 and 9.0 Hz, ArH), 7.12 (1H, d, J=1.8 Hz), 7.21 (1H, d, J=16.1 Hz, CH=CH), 7.42 (2H, d, J=8.8 Hz, ArH), 8.03 (1H, d, J=8.8, ArH), 10.80 (1H, s, OH).

6d: 2%; yellow orange crystals; mp 167—169 °C; EI-MS (m/z) 271 (M^+). Found: C, 66.43; H, 4.92; N, 5.17%. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.11%.

6′c: 13%; dark red crystals; mp 220—225 °C; EI-MS (m/z) 310 (M^+). Found: C, 69.69; H, 6.01; N, 9.01%. Calcd for $C_{18}H_{18}N_2O_3$: C, 69.66; H, 5.85; N, 9.03%. ^{1}H NMR δ=3.00 (6H, s, NMe), 6.49 (1H, d, J=15.6 Hz, CH=CH), 6.68 (2H, d, J=9.0 Hz, ArH), 6.76—6.99 (2H, m, CH=CH), 7.02 (1H, dd, J=1.5 and 8.8 Hz, ArH), 7.07 (1H, d, J=1.5 Hz, ArH), 7.09—7.13 (1H, m, CH=CH), 7.36 (2H, d, J=9.0 Hz, ArH), 8.02 (1H, d, J=8.8 Hz,ArH), 10.75 (1H, s, OH).

6′d: 9%; red needles; mp 171—172 °C; EI-MS (m/z) 297 (M^+). Found: C, 68.66; H, 5.11; N, 4.71%. Calcd for $C_{17}H_{15}NO_4$: C, 68.67; H, 5.08; N, 4.71%. ^{1}H NMR δ=3.83 (3H, s, MeO), 6.55 (1H, d, J=15.4 Hz, CH=CH), 6.76 (1H, d, J=15.4 Hz, CH=CH), 6.81 (1H, m, CH=CH), 6.89 (2H, J=8.8 Hz, ArH), 7.04 (1H, dd J=2.0 and 9.0 Hz, ArH), 7.10 (1H, d, J=2.0 Hz, ArH), 7.06—7.13 (1H, m, CH=CH), 7.41 (2H, d, J=8.8 Hz, ArH), 8.04 (1H, J=9.0 Hz, ArH), 10.74 (1H, s, OH).

6′e: 6%; yellow crystals; mp 145—147 °C; EI-MS (m/z) 267 (M^+). Found: C, 71.72; H, 5.02; N, 5.20%. Calcd for $C_{16}H_{13}NO_3$: C, 71.90; H, 4.90; N, 5.24%. ^{1}H NMR δ=6.61 (1H, d, J=15.6, CH=CH), 6.81 (1H, d, J=15.1 Hz, CH=CH), 6.93—6.99 (1H, m, CH=CH), 7.05 (1H, dd, J=1.5 and 9.0 Hz, ArH), 7.10—7.14 (1H, m, CH=CH), 7.13 (1H, d, J=1.5 Hz, ArH), 7.29—7.38 (5H, m, ArH), 8.05 (1H, d, J=9.0 Hz, ArH), 10.71 (1H, s, OH).

8h: 25%; red needles; mp 217—219 °C; EI-MS (m/z) 323 (M^+); IR 2200 ($C\equiv C$). Found: C, 81.72; H, 4.23; N, 4.33%, Calcd for $C_{22}H_{13}NO_2$: C, 81.72; H, 4.05; N, 4.33%. ^{1}H NMR δ=7.56 (2H, t, J=1.5 Hz, ArH), 7.65 (2H, t, J=1.5 Hz, ArH), 7.90 (2H, d, J=9.0 Hz, ArH), 8.06 (2H, d, J=8.0 Hz, ArH), 8.30 (2H, d, J=9.0 Hz, ArH), 8.52 (1H, s, ArH), 8.60 (2H, d, J=8.0 HZ, ArH).

9h: 14%; dark red crystals; mp 205—210 °C$_{\mathrm{decomp}}$; EI-MS (m/z) 339 (M^+); IR 2200 ($C\equiv C$). Found: C, 77.79; H, 4.11; N, 4.01%. Calcd for $C_{22}H_{13}NO_3$: C, 77.86; H, 3.86; N, 4.13%. ^{1}H NMR δ=7.32 (1H, dd, J=1.5 and 8.8 Hz, ArH), 7.51 (1H, d, J=1.5 Hz, ArH), 7.55 (2H, t, J=7.7 Hz, ArH), 7.64 (2H, t, J=7.7 Hz, ArH), 8.06 (2H, d, J=8.8 Hz, ArH), 8.16 (1H, d, J=8.8 Hz, ArH), 8.51 (1H, s, ArH), 8.57 (2H, d, J=8.8 Hz, ArH), 10.71 (1H, s, OH).

9i: 55%; red crystals; mp 189—191 °C; EI-MS (m/z) 339 (M^+); IR 2200 ($C\equiv C$). Found: C, 77.60; H, 4.16; N, 4.10%. Calcd for $C_{22}H_{13}NO_3$: C, 77.86; H, 3.86; N, 4.13%.

9j: 20%; pale yellow needles; mp 209—213 °C EI-MS (m/z) 240 (M^+); IR 2200 ($C\equiv C$). Found: C, 64.79; H, 3.60 N, 11.40%. Calcd for $C_{13}H_8N_2O_3$: C, 65.00; H, 3.36; N, 11.66%. ^{1}H NMR δ=7.14 (1H, dd, J=8.8 Hz, ArH), 7.34 (1H, d, J=1.5 Hz, ArH), 7.41 (2H, d, J=5.9, PyrH), 8.13 (1H, d, J=8.9, ArH), 8.66 (2H, d, J=5.9, PyrH), 10.62 (1H, s, OH).

9k: 27%; orange crystals; mp 174—176 °C; EI-MS (m/z) 283 (M^+); IR 2200 ($C\equiv C$). Found: C, 63.50; H, 3.30;

N, 4.87%. Calcd for $C_{15}H_9NO_5$: C, 63.61; H, 3.20; N, 4.95%. ^{1}H NMR δ=6.01 (2H, s, CH_2), 6.82 (1H, d, J=8.3 Hz, ArH), 6.99 (1H, d, J=1.5 Hz, ArH), 7.07 (1H, dd, J=1.5 and 8.8 Hz, ArH), 7.10 (1H, dd, J=1.5 and 8.3 Hz, ArH), 7.25 (1H, d, J=1.5 Hz, ArH), 8.07 (1H, d, J=8.8 Hz, ArH), 10.63 (1H, s, OH).

9l: 17%; yellow crystals; mp 215—220 °C; EI-MS (m/z) 300 (M^+); IR (C≡C) 2200. Found: C, 56.39; H, 2.89; N, 9.12%. Calcd for $C_{14}H_8N_2O_6$: C, 56.00; H, 2.69; N, 9.33%. ^{1}H NMR δ=7.11 (1H, dd, J=2.0 and 8.8 Hz, ArH), 7.20 (1H, d, J=8.8 Hz, ArH), 7.30 (1H, d, J=2.0, ArH), 7.74 (1H, dd, J=2.0 and 8.8 Hz, ArH), 8.15 (1H, d, J=8.8 Hz, ArH), 8.34 (1H, d, J=2.0 Hz, ArH), 10.62 (1H, s, OH), 10.74 (1H, s, OH).

10i: 4%; yellow needles; mp 163—165 °C; EI-MS (m/z) 341 (M^+).

ESR and Electrochemical Measurements A fresh bottle of reagent grade DMF was used for the reaction. For the electrochemical measurements, DMF was used after distillation over CaH_2 under reduced pressure. The ESR spectra were recorded by a JEOL FE2XG X-band spectrometer operating with 100 kHz field modulation. The magnetic field strength was calibrated on the basis of the hfcc value of $[(SO_3)_2NO]K_2$(13.0 gauss), and the microwave frequency was monitored by an Advantest TR-5211 digital frequency counter. Cyclic voltammograms (CV) were recorded by a Yanagimoto P-1000H Voltammetric Analyzer, equipped with a three electrode system; Pt-disk working electrode (2.0 mm diameter), Pt-wire counter electrode, and Ag/Ag$^+$ reference electrode. CV of **3b**, **3d—f**, and **4b—f** were recorded for DMF solutions containing tetrabutylammonium perchlorate (TBAP, 0.1 M) as a supporting electrolyte. For example, a pseudo reversible CV of **4b** was clearly observed. The formal redox potential of **4b** was estimated to be −1434 mV (vs. Ag/Ag$^+$), as a mean value of the reduction and oxidation peak potentials at −1491 and −1376 mV (vs. Ag/Ag$^+$), respectively. By the same procedures, the one-electron reduction potentials estimated for the above compounds were as follows: **3b**, −1522; **3d**, −1483; **3e**, −1463; **3f**, −1309; **4c**, −1425; **4d**, −1405; **4e**, −1385; **4f**, −1305 mV (vs. Ag/Ag$^+$). Well-defined oxidation peak potentials due to one-electron oxidation potentials of these compounds were not recorded, in the present condition. An optically transparent cell$^{12)}$ and an electrochemical-ESR cell$^{15)}$ were prepared and developed, with reference to previous papers.

The detection of hydrogen peroxide was accomplished according to the HPLC-CL method developed already by us.$^{11)}$

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